

**AFRL-ML-TY-TR-2007-4527**



# **FIRE FIGHTING AGENT RESEARCH – PHASE I**

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**April 2007**

**Interim Report for 1 September 2004 – 31 July 2006**

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<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b>						
<b>13. SUPPLEMENTARY NOTES</b>						
<b>14. ABSTRACT</b>						
<b>15. SUBJECT TERMS</b>						
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>	<b>18. NUMBER OF PAGES</b>	<b>19a. NAME OF RESPONSIBLE PERSON</b>	
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## ABSTRACT

This project's objective is to replace current firefighting aqueous film forming foams, AFFF, with an agent that is twice as effective at fire extinguishment. By reducing the required foam/water solution, the deployed firefighting footprint will thereby be reduced. In order to do this, the mechanism of firefighting foams and surfactants must be determined. Such physical characteristics as equilibrium surface tension, dynamic interfacial tension, and surface pressure have been examined in order to determine agent/surfactant behavior during the extinguishment process. This data will be correlated with computer models that will then be used to predict new, more efficient firefighting agents.

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# Advanced Agent Research – Phase I

## INTRODUCTION

This report describes the initial phase of a multiyear program designed to provide water based agents with fire extinguishing properties far superior to the incumbent Aqueous Film Forming Foam (AFFF). A new agent will be required to meet a variety of new challenges in terms of safety and environmental properties that were not considered historically in the development of new agents.

## Background

AFFF was developed by the Navy at Naval Research Laboratory in 1962<sup>1</sup>, in cooperation with the fluorosurfactants manufacturer, 3M. This material in water solution showed extraordinary performance in extinguishing hydrocarbon pool fires. The primary characteristic of that new foam was its ability to stabilize a thin film of water solution floating on top of various hydrocarbon fuels. This unusual behavior is the result of a balance of surface tensions and interfacial tensions providing the energy required to apparently defy the law of gravity. This property led to the informal description of the material as “light water”, which later became the 3M trademark for their brand of AFFF.<sup>2</sup>

During the next several years foam systems continued to use protein foams because of low cost. These foams relied on hydrolyzed meat packing wastes (horns, hooves and blood) to produce thick foams which extinguished fires by forming a thick foam blanket. This changed when the aircraft carrier Forrestal was nearly destroyed by a flight deck fire resulting from the accidental firing of a Zuni rocket<sup>3</sup>. This event convinced Navy and shortly later Air Force authorities to implement the development of a Military Specification (Mil Spec) and to conduct extensive testing to require the application of AFFF in all military aviation crash and shipboard applications. The performance estimates provided by Geyer<sup>4</sup> have become the basis for military, Federal Aviation Agency (FAA), International Civil Aviation Organization (ICAO) and National Fire Protection Association (NFPA) standard practices.

Recently, the fluorosurfactants used in the 3M formulations have been removed from production due to environmental concerns.<sup>5</sup> The fluorosurfactants used by the manufacturers of other brands of AFFF are currently being evaluated for environmental hazards.<sup>6</sup> Another fluorosurfactant, perfluoro-octanoic acid (PFOA) has recently become an object of environmental concern following the EPA’s Scientific Advisory Board (SAB) review of the draft hazard analysis of PFOA. The SAB review classified PFOA as a “likely human carcinogen.”<sup>7</sup>

## Purpose

This project is aimed at providing Air Force fire fighters with a superior extinguishing agent for application to large scale hydrocarbon fires resulting from aviation mishaps and other incidents where a reliable fire fighting agent is needed.

## **Scope**

This is an advanced research project using fundamental concepts derived from basic research to relate the molecular structure of water soluble or dispersible additives to the ability of the material to extinguish fires.

## **APPROACH**

At the most fundamental level the science of chemistry is built around the premise that the physical properties of all materials are determined by the composition and structure of the simplest unit, the molecule. This unit, when broken down to smaller pieces no longer can be multiplied to produce the bulk substance. These units may be small, such as water (H<sub>2</sub>O) or oxygen (O<sub>2</sub>); or very large such as proteins or other biological molecules. Combinations of molecules become complex systems such as oxygen dissolved in water or a drug destroying a virus.

During the first three quarters of the twentieth century chemists became adept in the use of quantum mechanical models to predict the properties of small molecules in isolation. Over the last thirty years new approaches have been developed that permit chemists, and now even biologists to predict the properties of the complex systems that are important in real world applications. The discussion of Computational Modeling, below provides an introduction to this technology.

## **Model Driven Discovery**

The application of computational modeling applied in this work can best be described as “Model Driven Discovery”.<sup>8</sup> Historically, models, or particularly Informal Qualitative Models (IQM) have provided the key insights which have led to discovery in chemistry and other sciences.<sup>9</sup> Today, computational capabilities have allowed development of quantitative models which can be used to make scientific discoveries. In fact, the tools of artificial intelligence<sup>10</sup>, data mining, molecular modeling and even life cycle modeling have become driving forces for discovery in the pharmaceutical industry<sup>11</sup>

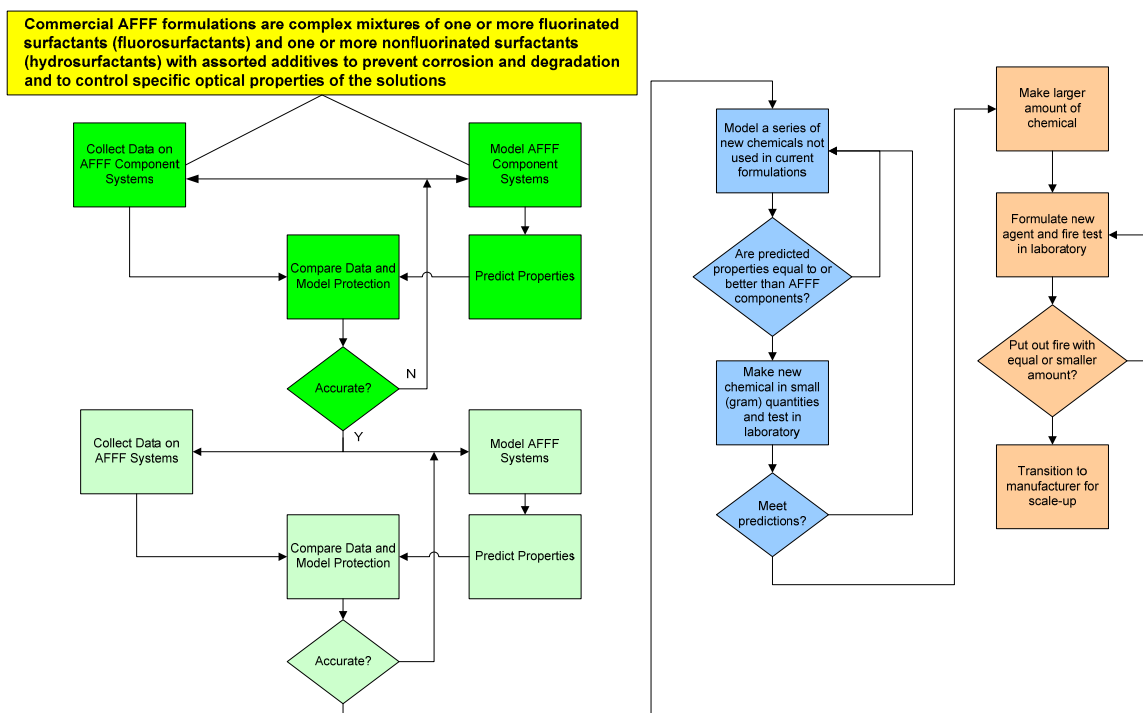
Figure 1 provides the conceptual model. This report provides a review of activities conducted as the first phase of the effort, bright green in the model diagram.

## **Benefits**

The driving force behind this approach is the limited funding available for this effort. By using this combination of molecular-modeling/molecular-dynamics (MM/MD) and small scale laboratory experiments AFRL/MLQ has minimized the risk associated with traditional new agent development. The cost of developing halon replacements under the Department of Defense, Technology Development Plan (TDP) was estimated to be \$160 million.<sup>12</sup> By the use of modeling, simulation and sensitive diagnostic tools the development and fielding of an improved performance replacement for AFFF can be accomplished in at a very small fraction of the cost involved in halon replacement.

## **Disadvantages**

The primary disadvantage of this approach is the amount of time required before an actual end use application can be experimentally verified. This requires a degree of management patience that is sometimes difficult to obtain.



**Figure 1. Flow chart of model directed advanced agent research program**

## COMPUTATIONAL MODELING

### Molecular Dynamics Simulation

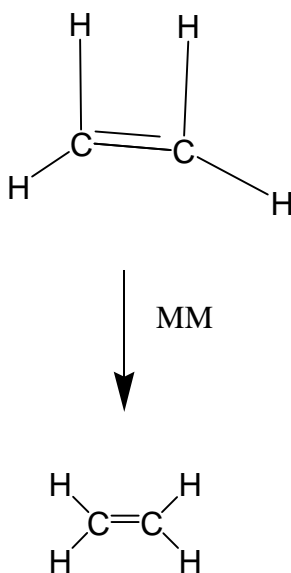
#### Theory

Computational chemical methods are being utilized to understand behavior of fire fighting agents in aqueous fire fighting foams. Modeling the behavior and properties of compounds in fire fighting agents such as perfluorinated surfactants in aqueous and/or organic solutions will aid in the understanding of the performance of fire fighting agents.

A wide range of theoretical methods exist which could be applied to modeling AFFF formulations. On one extreme are high level *ab initio* electronic structure calculations. These calculations use the laws of quantum mechanics to calculate properties of a system from a first principles approach. Such calculations offer the potential for very high accuracy but are very computationally expensive. Because of this expense, they are limited to systems on the order of a hundred atoms or so. Molecular modeling techniques on the other hand calculate properties of a system of atoms and molecules based on Newtonian mechanics. These calculations are therefore less accurate, but much larger systems can be studied because they are much less computationally expensive. At the other extreme of modeling techniques are meso-scale modeling methods. There, groups of atoms or even whole molecules are treated as single particles. For instance a surfactant molecule could be treated as a two particle system (one being the hydrophobic portion of the molecule, the other they hydrophilic). These calculations can simulate extremely large systems but rely on accurate parameterization of the constituents of the

system and cannot accurately model minor molecular changes to individual components. We have chosen to study AFFF formulations using the molecular modeling level of theory, which we believe represents the best compromise between accuracy and capability.

The molecular dynamics approach, which is an application of molecular modeling, is one promising technique. Very large simulations of up to many thousands of atoms can be carried out in a practical time frame. Molecular dynamics calculations are based upon molecular modeling techniques. In molecular modeling methods, a system of atoms and molecules is first described by defining their position in space and which pairs of atoms are bonded together. A force field, which is a set of mathematical equations and parameters that describe the interaction between bonded and non-bonded atoms, is then chosen. The molecular modeling program then evaluates the forces between atoms iteratively, and displaces the atoms so as to minimize these forces. Ultimately the minimal energy geometry of the atoms and molecules in the system is obtained. At that point the calculation ends and properties of the system are evaluated. The figure below illustrates a molecular modeling calculation on the molecule ethane. Here an initial arrangement of the atoms in the ethane molecule is refined by the molecular modeling technique until the equilibrium geometry is obtained.



**Figure 2. Illustration of a molecular modeling calculation on ethane.**

In a molecular dynamics simulation, the system is also allowed to propagate over time. This is done by defining a time step over which forces are evaluated. With each time step, the atoms in the system are displaced according to the forces acting on them and also based on the momentum they had from the previous time step. The system therefore possesses kinetic energy and physical properties such as temperature and pressure. A molecular dynamics simulation is usually allowed to continue for a certain number of time steps in order to model the behavior of the system for a certain amount of time. This

allows one to model the dynamic behavior of a system, from molecular vibrations to the diffusion of a molecule to the binding of a substrate to a protein.

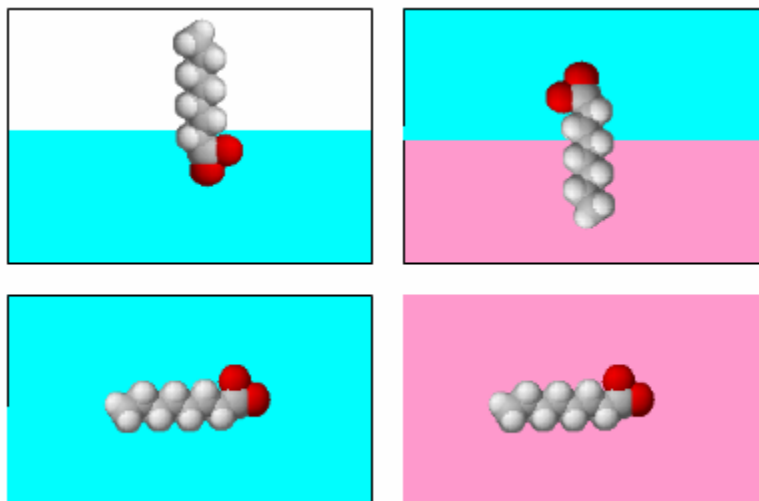
*Ab initio* and density functional methods may also be of use in this project. Although such calculations are limited to static properties of much smaller systems, they may be useful for calculating vibrational properties of molecules in order to obtain force field parameters, and for calculating interaction energies between surfactant and solvent molecules with a high degree of accuracy.

### **Simulation Goals**

Molecular dynamics calculations yield primarily qualitative information. One of the primary applications is in the area of biochemical simulations. For instance the user may be interested in observing the shape a protein assumes in an aqueous environment. Individual amino acids in a protein can be changed to observe how mutation changes the conformation of the protein; however, some quantitative information is also obtained in the process. For instance the total energy of the system can be calculated. This allows for such thermodynamic properties as binding energies, energies associated with conformational changes, and solvation energies to be estimated. In addition, some kinetic properties such as diffusion rates can potentially be obtained.

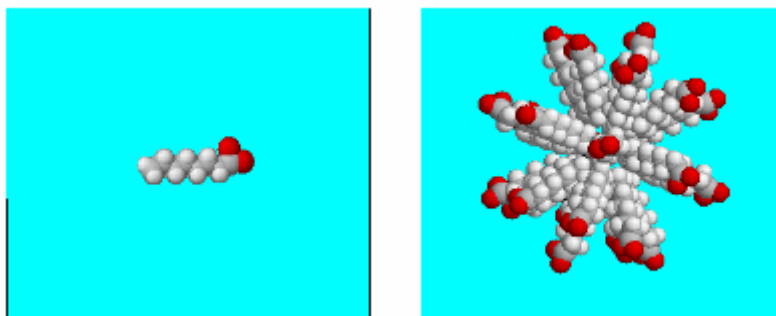
The goal of our molecular dynamics simulations of AFFF formulations is to understand how the surfactant and other ingredients of AFFF behave in air, water, and fuel environments and to use that knowledge to identify new, more effective agents. Put another way, we wish to identify those physical properties of AFFF agents that make them effective agents and use modeling and laboratory techniques to screen new candidate agents for effectiveness. The figures below depict different scenarios that can be modeled with molecular dynamics methods and illustrate some of the physical properties that can be obtained.

The first figure depicts a surfactant molecule in, and at the interface of, different chemical environments (white = air, blue = water, red = fuel). From such calculations, one can observe the geometric changes the molecule undergoes in these different environments, differences in total energies and therefore thermodynamics properties such as solvation energies and partition functions between different environments, and surface or bulk diffusion rates of the molecule in the different environments.



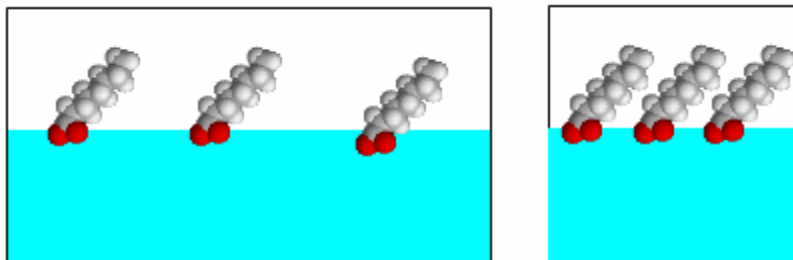
**Figure 3. Illustrations of a surfactant molecule in different chemical environments.**

The second figure depicts two simulations, one involving a single surfactant molecule in water, the second involving an aggregation of surfactant molecules into an aggregate structure, in this case a micelle. Aggregates of different sizes and arrangements can be modeled and from such calculations one can potentially obtain formation constants and critical micelle concentration (CMC) values for the surfactant.



**Figure 4. Illustration of a surfactant molecule in isolation and in an aggregate (micelle structure).**

The final figure depicts surfactant molecules at the air/water interface at different surface concentrations. Performing calculations on a surfactant molecule at a number of surface concentrations can potentially allow one to calculate surface properties such as the area per molecule at a saturated surface, as well as surface tensions and surface pressures at different concentrations.



**Figure 5. Illustration of surfactant molecules at different interfacial concentrations.**

The above illustrations depict some of the scenarios that can be modeled with molecular dynamics methods and list some of the physical properties that can be obtained. It remains to be seen whether such calculations can be carried out with sufficient accuracy and sufficient reproducibility to provide good correlation with experimental measurements and serve as a tool to evaluate the effectiveness of agents.

### **Software Evaluation**

#### **Molecular Dynamics Codes**

A large number of software packages are available for performance of molecular dynamics calculations. Many software packages were obtained for evaluation, including Amber<sup>13</sup>, CHARMM<sup>14</sup>, Chem 3D<sup>15</sup>, Materials Explorer<sup>16</sup>, Materials Studio<sup>17</sup>, NAMD<sup>18</sup>, and Tinker<sup>19</sup>. Molecular dynamics packages were evaluated on the basis of suitability for modeling surfactant/water/fuel systems. In particular, it was necessary to identify programs that allowed for the calculation of periodic systems containing on the order of one hundred thousand atoms. Most packages were found to be optimized for the calculation of biochemical, inorganic, or polymer systems. Some packages were found to be little more than molecular modeling packages with only limited dynamics capabilities. Others performed very poorly on systems of the size we are interested in.

#### **Materials Studio**

The commercial program Materials Studio, sold by Accelrys, is something of an industry standard for the molecular dynamics simulation of periodic inorganic and polymer systems. It has a very attractive user interface and contains the Cerius force field, a high quality force field that includes well developed parameters for the element fluorine. Unfortunately several factors ruled out its use in our study. The attractive interface is provided for the Windows operating system only, and exporting data to a UNIX platform for calculations proved to be awkward. The Cerius force field is proprietary data stored within the program in binary format. Extending or modifying the force field is not possible. The program itself is quite expensive. The most limiting factor was the poor performance of the code on systems of more than a few hundred atoms, and an imposed limit of a few thousand atoms on the size of the system. These factors ruled out Materials Studio from use in our project.

## NAMD

The molecular dynamics package NAMD, produced by The Theoretical and Computational Biophysics Group (TCBG) of the NIH Resource for Macromolecular Modeling and Bioinformatics, is another widely used code. NAMD has several features that make it an attractive code for our purposes: It is capable of modeling very large systems on the order of a hundred thousand atoms. It performs well on multiprocessor computing systems. It includes an attractive GUI in the form of an external program named VMD, which is capable of monitoring calculations in real time. It accepts many different force fields including user defined parameters. Finally it is freely available, open sourced, and well documented. For these reasons, NAMD was chosen to perform our molecular dynamics investigation of AFFF systems.

## **Visualization Programs**

Unlike Materials Studio and NAMD, most molecular dynamics codes do not come with efficient visual interfaces. In those cases it is necessary to obtain an additional visualization program in order to aid in setting up a simulation, observing the simulation as the calculation proceeds in real time, visualizing the final results of the calculation, and preparing graphic images for reports and presentations. Fortunately there are a large number of free visualization programs available that offer high quality graphics and a range of capabilities.

Since we have chosen to use the program NAMD for our molecular dynamics calculations, the program VMD has been used for the majority of our visualization needs. One attractive feature of VMD is that the program is extensible with the use of python scripts. One feature that we have added to VMD by this method is the ability to draw a box to illustrate the unit cell size in calculations that utilize periodic boundary conditions. This has proved very useful when preparing initial starting conditions for a calculation.

Another visualization program that has proved of use is the program RasMol, a freeware visualization program created by Rodger Sayle. RasMol has far fewer features than VMD has, however RasMol is very fast due to its lower quality graphics and low system requirements. This makes it very handy when large numbers of files need to be examined quickly.

## **Auxiliary Programs**

There has been occasional need for calculations at the *ab initio* level of theory for this project. There are relatively fewer *ab initio* packages available than molecular dynamics packages. However, most are very similar in capabilities and use. The free package GAMESS and the commercial package Gaussian have been obtained for our systems. The Gaussian suite has already been used to test the quality of fluorine force field parameters. Having access to these codes will prove useful if generation of new force field parameters becomes necessary.

Several other programs have proved to be very useful in the creation and manipulation of input and output files. The program OpenBabel, a freeware product of the OpenBabel team, is a program used to convert between many different file formats common to computational chemistry. The program BMol, a freeware program developed by Bernard Heymann, is very useful for manipulating, combining, and editing PDB format files, a

common file format in molecular dynamics calculations. The program Vega is a freeware program developed by the Drug Design Laboratory, Medicinal Chemistry Institute, of the Milan University, is another program useful for manipulation PDB files.

## **Force Field Evaluation**

### **Existing Force Fields**

A force field is a set of mathematical equations and parameters describing the interaction between atoms as well as a set of parameters that are obtained through experimental methods or high level calculations. For instance the term used to describe the interaction between two atoms that are bonded together is:

$$E_{bond} = K \times (R - R_0)^2$$

### **Equation 1**

Where R is the current distance between the two atoms,  $R_0$  is the equilibrium distance between the two atoms, and K is a force field parameter that is dependant on the identity of the two atoms. Other terms commonly encountered in force fields include a term describing the interaction between two atoms that are not bonded together, and a term describing the interaction between two atoms bonded to a third common atom. Many other terms are possible. Different force fields can include terms for many different types of interactions, and may even have different equations describing the same physical interaction. Even if the form of the potential is the same, different force fields will have different fitting parameters (the K in the above equation) which make transferring parameters between force fields inadvisable.

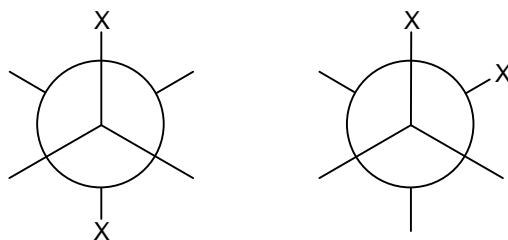
Many difference force fields are available, and most molecular dynamics packages are capable of using many different force fields. One source of confusion is the fact that developers often give the same name to both a molecular mechanics program that they create as well as to a force field that they develop. (I.e. Amber, CHARM, etc.) Several different force fields, including Amber, CHARMM, Compass, MM2, MM3, MMX, OPLS, and OPLS-AA were evaluated for applicability to our systems of interest. One limitation is the fact that most existing force fields are intended for use in modeling biological systems. Therefore, they usually provide force field parameters for a limited set of elements. Many did not include parameters for the element fluorine at all, making them of little use for our systems of interest. Others contained rudimentary parameters of very poor quality. The figure below shows a periodic table where those elements that are well developed in a typical force field are colored green. Notice that the only halogen that is typically developed is chlorine. Even in that case, parameters are usually only developed for the chloride ion, rather than for chlorine covalently bonded to carbon or other atoms.



## Generating New Force Field Parameters

Developing new force field parameters is a relatively straightforward but time consuming procedure. Force constants for a representative set of molecules are first obtained by experimental measurements or quantum chemical calculations. These force constants cannot usually be used “as is” but must be scaled to make them compatible with existing parameters in the force field in question. This is done using an iterative procedure in which parameters are gradually altered until some physical property, usually a molecular geometric or energetic quantity, is matched. Electrostatic parameters must be obtained by quantum mechanical calculations or by fitting as no experimental techniques exist to directly measure partial atomic charges.

Developing force field parameters for the element Fluorine is potentially very difficult. This is due to the nature of molecular mechanics type force fields, where atoms are treated as objects that obey Newtonian mechanics. Concepts such as lone pair electrons or bond conjugation in aromatic rings is difficult to model accurately with such terms since they are due to electronic effects. Interactions involving fluorine atoms (the most electronegative element) also rely to a considerable extent on electronic effects. An example is the so called Gauche Effect. The figure below shows two conformations of a di-substituted ethane molecule. Based only on Newtonian mechanics, where steric effects would predominate, the trans conformation (left) would be the preferred conformation. This is indeed the case for most constituents. However, when the constituents are very electronegative, such as fluorine atoms, then the gauche conformation is preferred. It may be difficult to develop high quality fluorine parameters that reproduce these effects.



**Figure 8: Venn diagram showing the trans (left) and gauche (right) conformations.**

As mentioned above, force field parameters for the element fluorine are rudimentary or non-existent in most force fields. If parameters of sufficient quality are not identified, then it may become necessary to develop new force field parameters ourselves.

### The CHARMM Force Field.

The CHARMM force field, developed by Alexander D. MacKerell Jr. et al., is a widely used force field in molecular modeling. Like most force fields, it has been developed with biochemical applications in mind. It is distributed with parameters for proteins, DNA and RNA chains, lipids, and sugars. It also has a library of small molecules, including hydrocarbons, which is easily extended to include molecules such as octane or benzene that can be used as the hydrocarbon fuel layer in our systems. It comes with the NAMD distribution and is the default force field so it is somewhat natural to attempt to

use it in our simulations. Initial simulations with the CHARMM force field, discussed later in this report, show that it provides qualitatively accurate results and suggest that with minor improvements it may provide quantitative agreement with experiment.

Until recently the CHARMM force field had no parameters for the element fluorine. For most of this project, fluorine parameters taken from the Amber force field were used with the CHARMM force field in order to perform proof of concept calculations on fluorine containing systems. These parameters were modified with scaling factors obtained from a correlation plot of those parameters which the two force fields have in common. Different scaling factors were obtained for each term in the force field potential.

The most recent release of the CHARMM force field, version 31 beta 3, includes force field parameters for the element fluorine that were developed by Chen, Yin, and MacKerell. These parameters appear to be more extensive and further optimized than those present in the Amber force field. We are in the process of evaluating these new CHARMM parameters for use in our systems.

### **Input File Generation**

Preparing input files for a molecular dynamics simulation is a non trivial matter. NAMD, like most molecular dynamics programs uses modified PDB (Protein Data Bank) format files as its input format. The PDB file format was developed by the biochemical community and the x-ray crystallography community for the description of proteins and other biological molecules. A large number of PDB files are available from the Protein Data Bank web site ([www.rcsb.org/pdb](http://www.rcsb.org/pdb)). PDB files are text files. A sample PDB file describing a system of three water molecules is shown below:

HETATM	1	H	UNK	1	0.583	-0.458	0.000	1.00	0.00	H
HETATM	2	H	UNK	1	-0.583	0.458	-0.000	1.00	0.00	H
HETATM	3	O	UNK	1	-0.359	-0.458	0.000	1.00	0.00	O
HETATM	4	H	UNK	2	5.583	-0.458	0.000	1.00	0.00	H
HETATM	5	H	UNK	2	4.417	0.458	0.000	1.00	0.00	H
HETATM	6	O	UNK	2	4.641	-0.458	0.000	1.00	0.00	O
HETATM	7	H	UNK	3	2.583	2.542	0.000	1.00	0.00	H
HETATM	8	H	UNK	3	1.417	3.458	0.000	1.00	0.00	H
HETATM	9	O	UNK	3	1.641	2.542	0.000	1.00	0.00	O
CONECT	1	3								
CONECT	2	3								
CONECT	3	1	2							
CONECT	4	6								
CONECT	5	6								
CONECT	6	4	5							
CONECT	7	9								
CONECT	8	9								
CONECT	9	7	8							
END										

The first nine rows, which begin with HETATM, each describe one of the atoms in the system. The second group of rows, that begin with CONECT, specify which atoms are chemically bonded together. PDB files can be created from scratch with a simple word processor. However this becomes impractical for systems with more than a few atoms. PDB files can also be created with many chemical drawing programs, such as Chem3D by Cambridge Software.

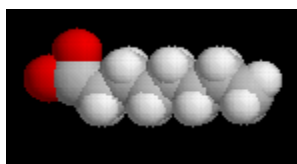
Unfortunately most molecular dynamics programs do not accept files in normal PDB format; they must be modified slightly to make them useable. The above PDB file, modified to work with NAMMD, is shown below:

ATOM	1	H1	TP3M	1	0.583	-0.458	0.000	1.00	0.00	SOLV
ATOM	2	H2	TP3M	1	-0.583	0.458	-0.000	1.00	0.00	SOLV
ATOM	3	OH2	TP3M	1	-0.359	-0.458	0.000	1.00	0.00	SOLV
ATOM	4	H1	TP3M	2	5.583	-0.458	0.000	1.00	0.00	SOLV
ATOM	5	H2	TP3M	2	4.417	0.458	0.000	1.00	0.00	SOLV
ATOM	6	OH2	TP3M	2	4.641	-0.458	0.000	1.00	0.00	SOLV
ATOM	7	H1	TP3M	3	2.583	2.542	0.000	1.00	0.00	SOLV
ATOM	8	H2	TP3M	3	1.417	3.458	0.000	1.00	0.00	SOLV
ATOM	9	OH2	TP3M	3	1.641	2.542	0.000	1.00	0.00	SOLV
END										

Several changes were made in converting the PDB file. The CONECT lines aren't needed and were removed. The atom specifications "H" and "O" were changed to "H1", "H2", and "OH2". This is necessary because each atom in a molecule must have a unique specification. The molecular specification was changed from "UNK" (unknown) to "TP3M" (water). Each molecule, and many molecular fragments such as protein residues, must have a particular designation. Finally, a new column "SOLV" (for solvent) was added which is just a descriptive designation but must be present.

Making all these changes to a large PDB file with a word processor would be impractical, and no programs exist that perform these changes. It was therefore necessary to develop a procedure that would allow us to create a molecular dynamics compatible PDB file from scratch. Below we will describe the procedure for creating an input file for performing a simulation on a micelle type cluster of surfactant molecules solvated by water. We will use perfluorinated octanoic acid (PFOA) as the surfactant for this example.

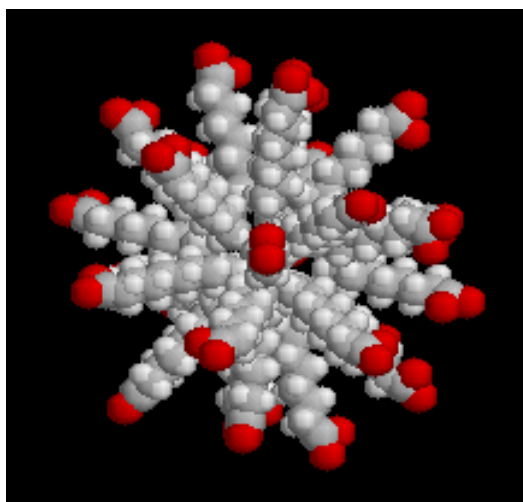
The first step is to use a program such as Chem 3D to generate PDB files for the individual molecules that are in the system of interest. In this case we create a PDB file for water and another for PFOA. An illustration of PFOA is shown below.



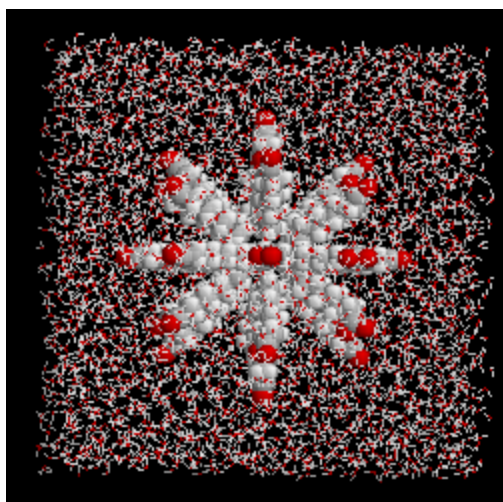
**Figure 9: Perfluorinated octanoic acid (PFOA).**

The PDB file generated by Chem 3D is in standard format and will need to be modified as described above. However this is simple to do as it contains a small number of atoms. Likewise with the water PDB file.

Now that we have PDB files for single molecules in the correct format, we need to duplicate the surfactant molecule and combine them to create a single PDB files that describes the micelle cluster. Care must be taken to only use a program that does not change the files back into standard PDB format. This can be done with some graphical programs such as VMD. However, when using a graphical program each molecule must be copied and moved one at a time which makes creating very large systems very time consuming. The program BMol was found to be better suited for this purpose. BMol has a text based interface, which permits the user to move or rotate a molecule by a specified distance or angle. Furthermore it is simple to create text files containing scripts of BMol commands. This makes it very easy to generate large, complex structures with little effort. Using BMol we can thus copy, rotate, move, and combine our initial PFOA molecule several times until we have a single PDB file that describes a micelle type structure, shown below. Notice that BMol allowed us to generate a very symmetric and complex geometric shape, which would be difficult to do “by hand” using a GUI to move molecules one at a time.



**Figure 10: Several PFOA molecules grouped into a micelle structure.**



**Figure 11: A cluster of PFOA molecules solvated by water molecules.**

We could then repeat this procedure to place water molecules around the micelle. Alternately, we can prepare a box containing just water molecules and use BMol to place the micelle into the box, while removing those water molecules that happen to overlap the PFOA molecules in the micelle. Either way, we obtain the structure shown below:

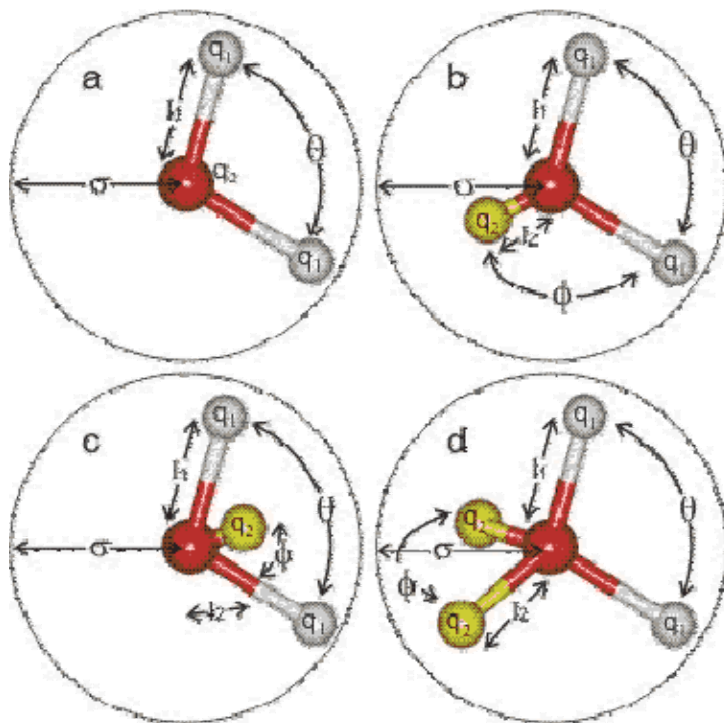
By following this procedure we obtain a PDB file that is compatible with NAMD or other molecular modeling programs. With minor modifications we can form other arrangements of surfactant molecules such as films at an interface. Fuel layers can be created by using an organic molecule such as benzene or octane rather than water. Later in this report we will describe a number of model systems that have been created using this procedure.

### **Simulation Validation.**

Before proof of concept calculations were done on large surfactant/water/fuel systems,



**Figure 12: The sixteen processor Linux cluster purchased in order to perform calculations for this and other projects.**



**Figure 13: Illustration of several models of the water molecule. Model “C” illustrates the TIP3M model.**

smaller calculations were performed to verify that our simulation methods were producing reasonable results. These calculations served as a “sanity check” to insure that the methods were at least producing qualitatively accurate results and deserve further refinement to improve their quantitative accuracy.

In order to perform these and other molecular dynamics calculations, our group purchased a Beowulf Linux cluster from Aspen Systems, Inc. This system contains eight nodes, each node having two 2.8 GHz processors and 2GB of memory, as well as support components including a UPS, and Ethernet & KVM switches. A picture of the cluster is shown Figure 12.

### **Water Clusters.**

Perhaps the simplest model simulation conceptually is a cluster of water molecules. However in practice accurate molecular dynamics simulations on water clusters are

extremely difficult. One reason is that water molecules constantly undergo hydrogen exchange, where water molecules hydrogen bond with each other and then exchange protons, as well as forming species such as  $\text{OH}^-$ ,  $\text{H}_3\text{O}^+$ , and other more complex species. These processes are impossible to model with chemical dynamics, which cannot model any processes or reactions where bonds are formed or broken. In addition the electronic structure of water with its two electron lone-pairs causes it to have very complicated interactions with nearby molecules. It is often necessary to include additional, massless, point charges in the three atom water molecule to reproduce these effects. The figure below illustrates some of the molecular modeling approximations for the water molecule. Model “a” is the simple three body model for water. Models “b” and “c” include one additional, massless point charge in the plane of the water. Model “d” includes two point charges, out of the plane of the water molecule, in the locations that are typically associated with the water lone-pair electrons.

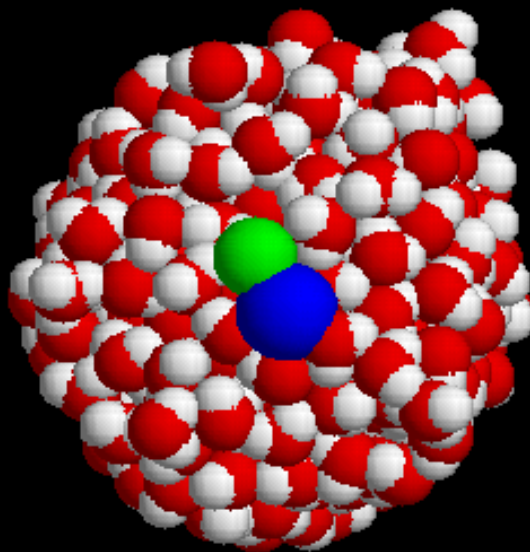
In our calculations thus far, we have chosen to utilize the TIP3M model for the water molecule. The TIP3M model uses the scheme depicted in part “c” in the above figure. This model has been optimized to more accurately reproduce the bulk properties

of water than the simple three body model. The TIP3M model of water is included in the CHARMM force field, and NAMD has been optimized so that it performs calculations with this particular water model very efficiently.

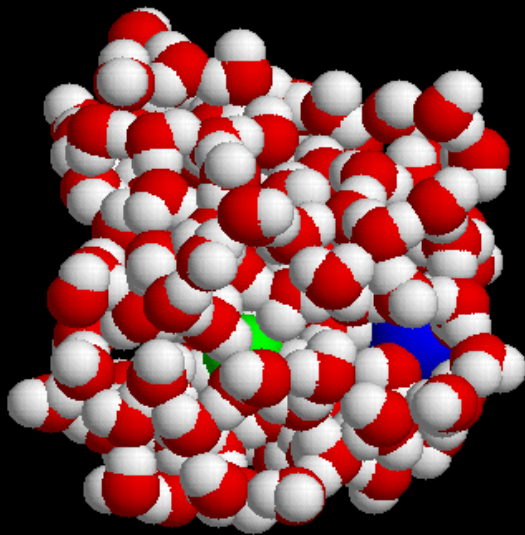
A number of calculations were performed on simple water droplets and periodic systems of pure water to evaluate the accuracy of the TIP3M water model and other parameters in our simulations. The results were in satisfactory agreement with experimental values for bulk properties of water. The water molecules were observed to prefer to orient themselves so that hydrogen atoms on one molecule were oriented toward oxygen atoms of neighboring molecules so as to maximize hydrogen bonding.

#### Aqueous Salts.

A more complex test was performed by adding one

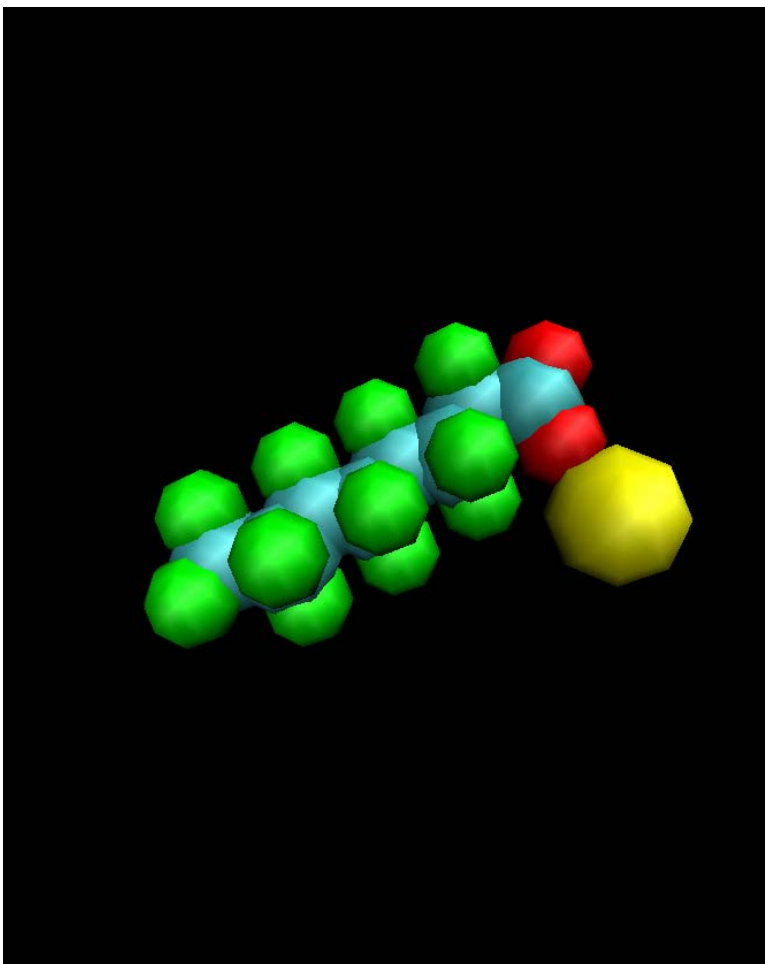


**Figure 14: A molecular dynamics simulation of a water droplet containing one sodium atom and one chlorine atom using the MM2 force field.**



**Figure 15: A molecular dynamics simulation of a water droplet containing one sodium atom and one chlorine atom using the CHARMM force field.**

sodium ion and one chlorine ion to the water droplet. Here very different results were observed depending on the quality of the force field. The figure below illustrates the results of a calculation using the MM2 force field, a relatively poor force field. Here the two ions remained in close proximity to each other during the course of the simulation. Attractive forces between the water molecules and the ions were not enough to overcome the coulombic attraction between the ions. In addition the two ions remained on the surface of the droplet, rather than being solvated and pulled toward the interior of the droplet.



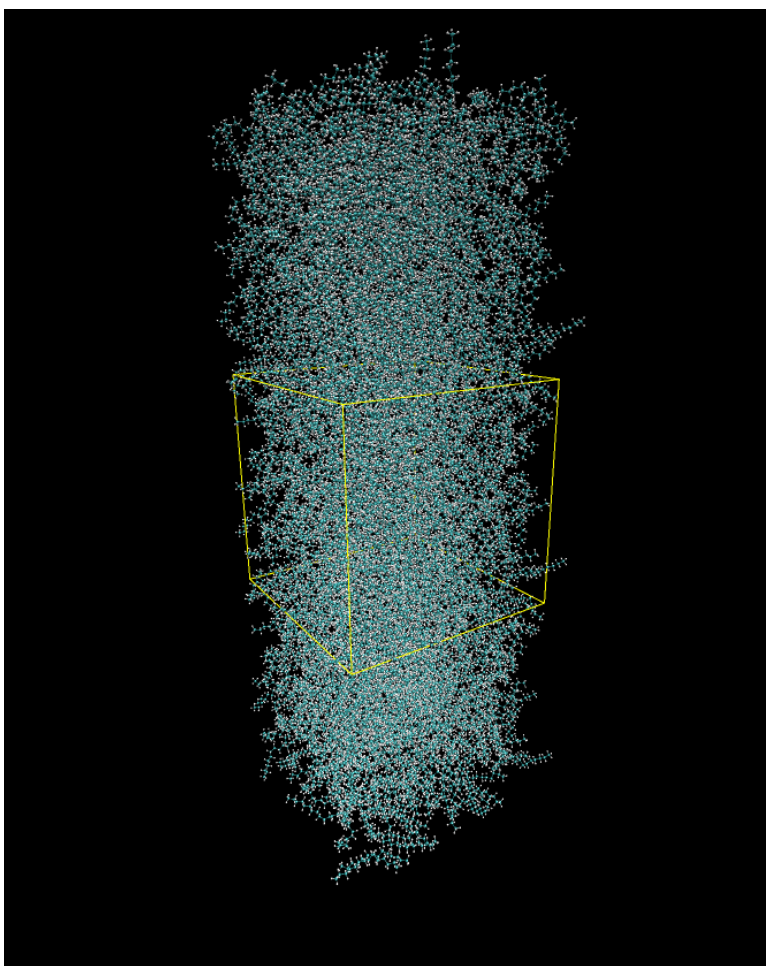
**Figure 16: The geometry of Sodium PFOA produced after a molecular dynamics simulation.**

The figure below shows the same system, this time modeled using the CHARMM force field. This calculation produced results much more in line with what our chemical intuition expects. The ions were pulled apart and solvated by the water molecules, which surrounded the ions and pulled them into the interior of the droplet.

This series of calculations was one of the first we attempted that illustrated the dramatic difference in results that can be obtained using force fields of different quality. The CHARMM force field with the TIP3M model for water was one of the few force fields that produced the expected results.

### **Ionic Surfactants**

Many if not most of the surfactant molecules we are interested in studying possess charged hydrophilic groups and a corresponding counter ion. Although in many cases the surfactant and counter ion will be solvated by water molecules and well separated from each other, interaction between these two species will still occur. The figure below illustrates the final geometry obtained from a molecular dynamics simulation of sodium perfluoro octanoic acid in the gas phase. During the course of the simulation, the sodium ion remained coulombically attracted to the oxygen atoms in the polar head group. This simulation was performed at a simulation temperature of three hundred degrees Kelvin. At significantly higher temperatures, the extra kinetic energy caused the sodium ion to disassociate itself from the PFOA fragment. We did not attempt to identify the exact temperature where disassociation occurred, as it was beyond the temperature at which chemical bond breaking is likely to occur.



**Figure 17: Result from a simulation of tetradecane using periodic boundary conditions. The unit cell is shown as a yellow box. The contents of replicated cells above and below the unit cell are also shown.**

### Periodic Systems.

The use of periodic boundary conditions permits the simulation of an infinite system by reproducing a discrete system defined by a unit cell (usually cubic) periodically along one or more axis. Atoms and molecules in the real unit cell are duplicated, or mirrored, in each duplicate, or virtual cell. Molecules which move across the boundary from the real into a virtual cell become virtual, mirrored molecules, while simultaneously a virtual molecule will cross the opposite boundary into the unit cell and become a real molecule.

The ability to perform simulations on systems with periodic boundary conditions is essential for many of the environments that we wish to model. For instance we desire to simulate the behavior of a

surfactant in the bulk water phase. We could try to do this by placing a surfactant molecule in a water droplet, but the surfactant molecule might diffuse to the surface of the droplet and remain there. A better solution would be to create a cube of water molecules and containing one surfactant molecule, then use periodic boundary conditions to mirror this cube in each direction. This way there would be no surface for the surfactant molecule could diffuse to. The size of the cube would have to be large enough to insure no interaction between surfactant molecules in adjacent cubes occurred. Unit cells with dimensions such that the distance between real particles and corresponding virtual particles are several times the columbic cutoff threshold are usually sufficient.

The figure below illustrates the results of a molecular dynamics simulation on bulk tetradecane ( $C_{14}H_{30}$ ) using periodic boundary conditions. The yellow cube represents the actual simulation space defined by the PDB file. The program simulated an infinite system by reproducing this cell along each axis. Also shown in the figure are the contents of the first mirrored cells above and below this cell.

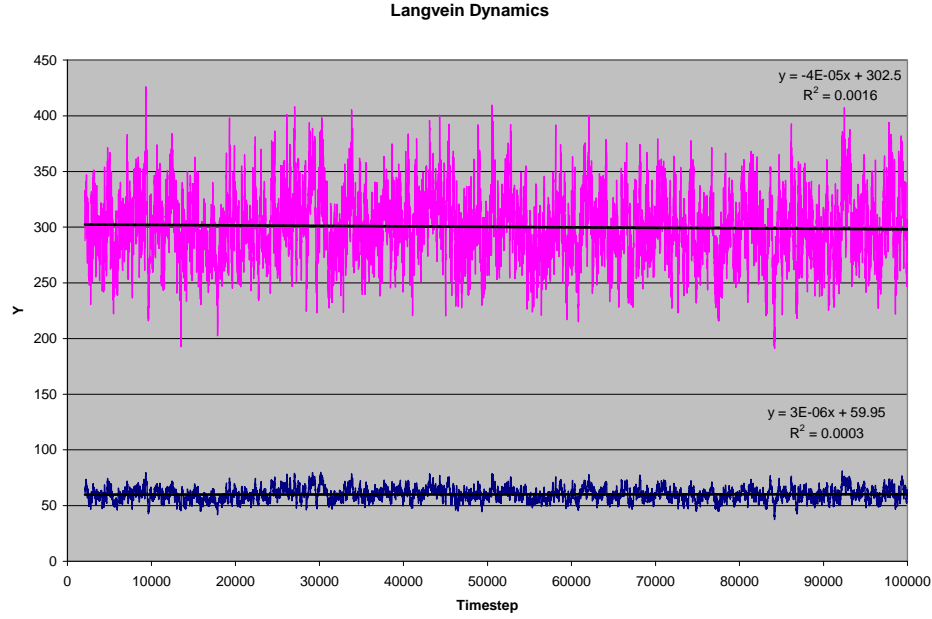
### **Constant Temperature Simulations.**

One of the parameters that are defined in a molecular dynamics simulation is temperature. The desired temperature is defined by the user at the start of each simulation, but from that point the temperature may vary during the course of the simulation. This is because the temperature is largely determined from the kinetic energy of the atoms in the system, and the kinetic energy is determined by the velocity of the atoms in the system. The velocities of the atoms in the system will change during the course of the simulation as the forces upon the atoms change. Also, a poor choice for the initial positions of the atoms can impart very large forces and therefore very large velocities to the atoms.

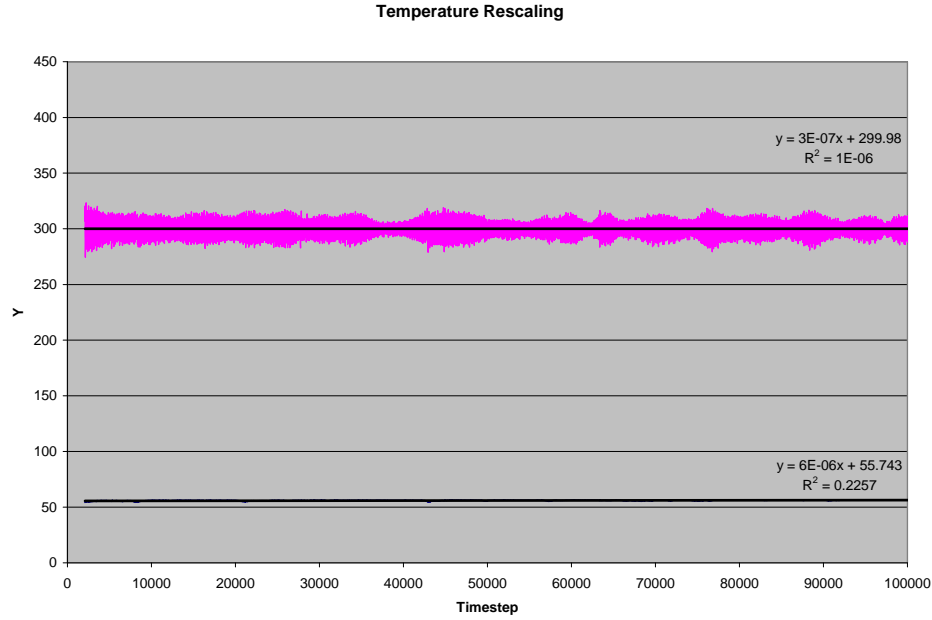
Various methods are often employed to insure that the simulation maintains the system at a constant temperature. These methods also give the user the ability to control the temperature during the simulation, for instance starting at one temperature, increasing the temperature over time to a new temperature, and then holding at the new temperature for the remainder of the simulation. For our purposes we will generally be interested in maintaining the temperature at a constant value for the duration of the simulation. In most cases we will be interested in maintaining the system at room temperature, which is usually defined as 300 degrees Kelvin for convenience.

NAMD includes two primary methods for temperature control, Langevin dynamics and temperature rescaling. In Langevin Dynamics, the temperature of the system is calculated periodically, and if the temperature does not match the desired temperature then the velocity of randomly chosen atoms is changed by a small amount in order to bring the temperature of the total system to the set point. In temperature rescaling, a similar procedure is followed. However, when the actual temperature of the system is found to deviate from the desired temperature, the velocities of all the atoms in the system are scaled so as to bring the system back to the desired temperature.

Several simulations were carried out using both Langevin dynamics and temperature rescaling. Identical systems were simulated using both methods, and the temperature and total energy were plotted to observe how well both quantities were maintained. The figures below show plots of temperature (red) and total energy (blue) vs. time for simulations of bulk tetradecane using these two methods.



**Figure 18: Plots of temperature and total energy for a simulation using Langvein Dynamics for temperature control.**



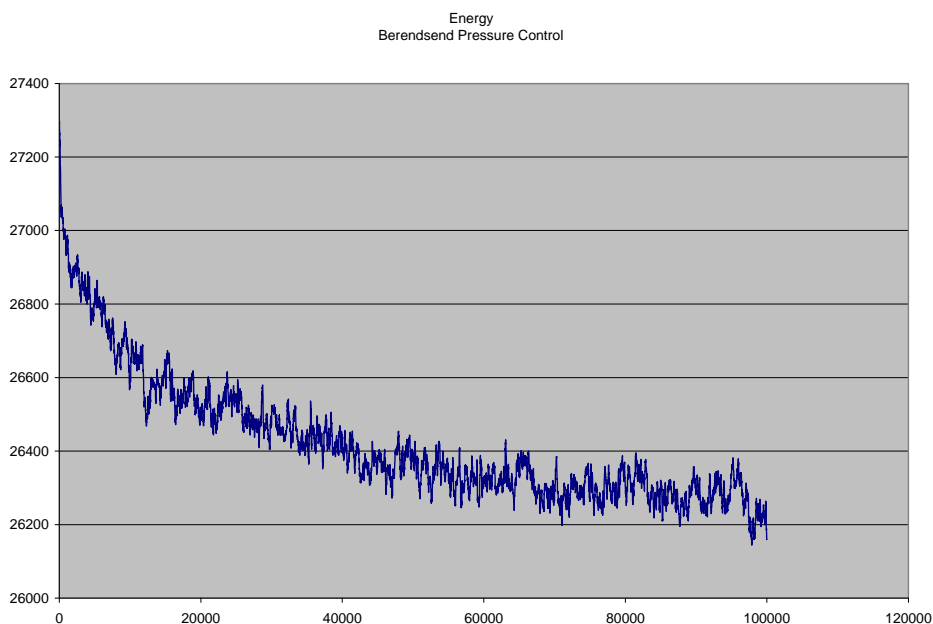
**Figure 19: Plots of temperature and total energy for a simulation using Temperature Rescaling for temperature control.**

For this system and all other systems studied, the temperature rescaling method did a better job of maintaining the system at constant temperature and energy. In particular temperature rescaling produced noticeably smaller deviations in the total energy of the system. In addition, when a gas phase system was modeled, the Langvein dynamics

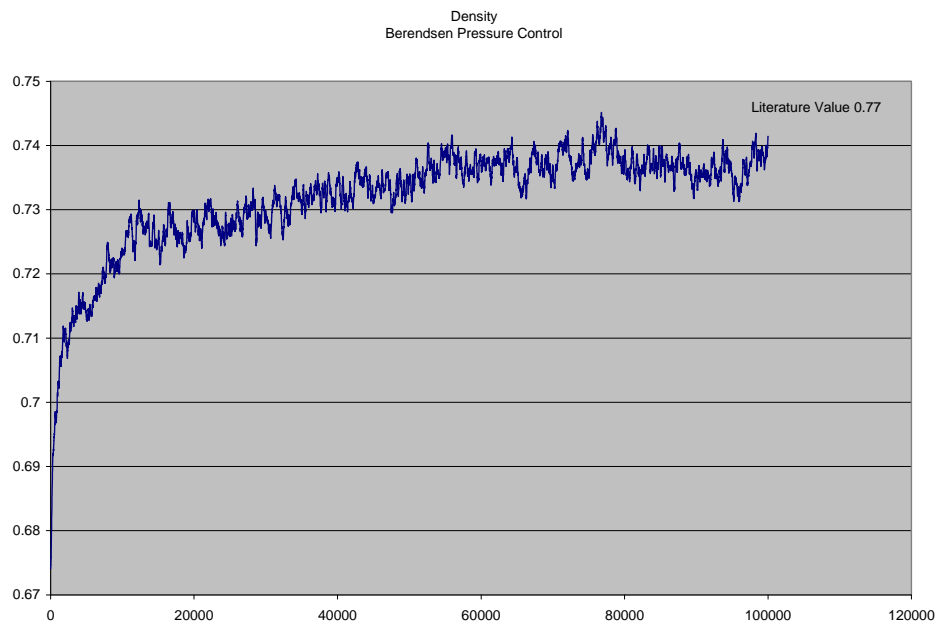
methods had a tendency to so perturb the system with constant adjustments that the gas molecules followed very chaotic trajectories rather than linear trajectories as would be expected. This deficiency was not observed with temperature rescaling. We have therefore chosen to use the temperature rescaling method for our systems of interest.

### Constant Pressure Simulations.

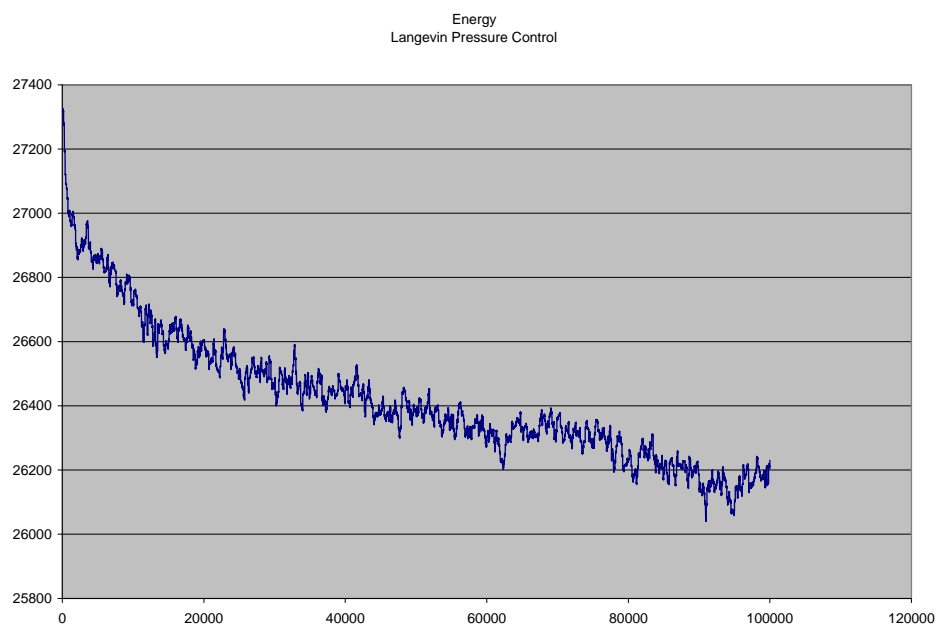
Like temperature, pressure is a defined quantity in molecular dynamics simulations, but only when the system is modeled with periodic boundary conditions. It is often the case that the user will be interested in maintaining the system at a constant pressure, usually 1.0 atmosphere (1.01325 bar). This is done by altering the dimensions of the unit cell (and therefore the volume) while maintaining the system at a constant temperature ( $P = nRT/V$ ). All three dimensions can be altered, either independently or proportionally to maintain constant ratios. NAMD has two primary methods for maintaining a system at a constant pressure, Berendsead pressure control, and Langvein pressure control. As in the case above for temperature control methods, we have run a number of simulations to evaluate the two methods of pressure control. Identical systems were simulated using both methods, and the pressure and total energy were plotted to observe how well both quantities were maintained. The figures below show plots of energy and density vs. simulation time for a simulation of bulk tetradecane.



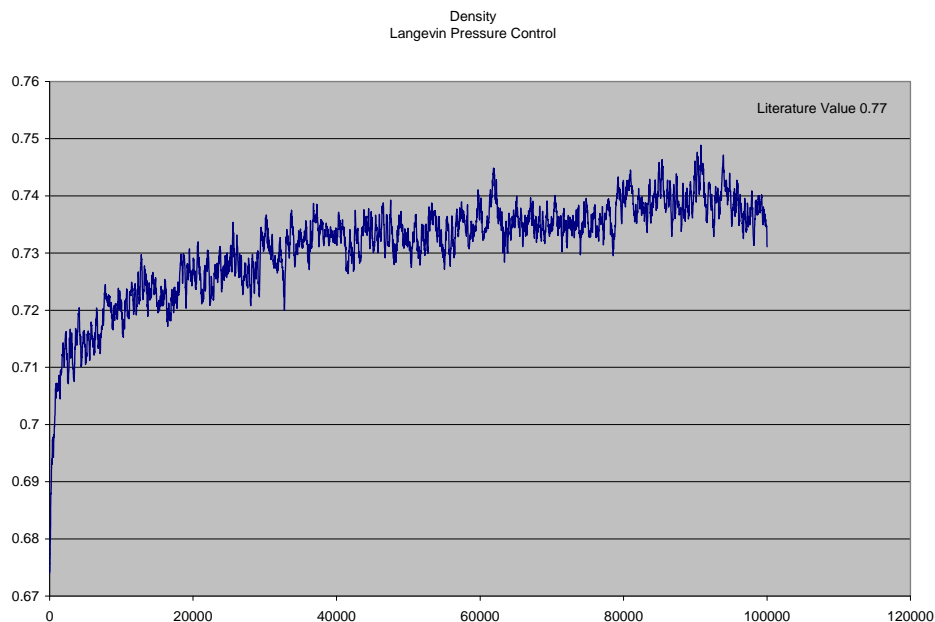
**Figure 20: Plot of total energy for a simulation using Berendsead pressure control.**



**Figure 21: Plot of density for a simulation using Berendsen pressure control.**



**Figure 22: Plot of total energy for a simulation using Langevin pressure control.**



**Figure 23: Plot of density for a simulation using Langevin pressure control.**

In this case neither simulation converged on a constant energy after one hundred thousand time steps. However, in this and all other systems for which the comparison was made, the Berenstead method appears to be converging more rapidly towards a limiting value. The Berenstead method also comes much closer converging on a constant density. By fifty thousand time steps, only very minor changes are being made to the unit cell size. We have therefore decided to use the Berenstead method for pressure control in a stepwise manner. First the system will be simulated using Berenstead pressure control until the density appears to be converging. Then the cell size will be fixed and the simulation allowed to proceed until the energy appears to converge. After that point, the simulation will be allowed to continue and qualitative and quantitative data will be collected.

### **Model Calculations**

The rationale discussed above was used to prepare and run a number of model simulations. These were intended to be proof of concept simulations to demonstrate that the different scenarios that were discussed above could be created using the methods we described for input file generation, and then simulated using NAMD.

A typical input script for the program NAMD is shown below. This particular simulation utilizes temperature rescaling to maintain a constant temperature of three hundred degrees, a constant pressure of one atmosphere, and periodic boundary conditions with a rectangular unit cell that is sixty angstroms on each side. Other simulation parameters can be read from the script. In most cases, default values were used for the remaining parameters. This script would be modified depending on the actual system we wish to model, i.e. if no periodic boundary conditions were required the appropriate sections would be modified or removed.

```

# constants
set temperature      300

# Input Files
coordinates          input.pdb
parameters            parameters.inp
paraTypeCharmm       on
structure             input.psf

# Output Files
binaryOutput         no
dcdFreq              100
dcdUnitCell          yes
outputName            z-out

# Standard Output
outputEnergies        10
outputTiming          0

# Timestep parameters
stepsPerCycle         10
timestep              1.0

# Simulation Space Partitioning
cutoff                12
pairListDist          13.5
switchDist            8
switching              on

# Basic Dynamics
1-4scaling            1.0
excludescaled1-4
temperature            $temperature

# Temperature Rescaling Parameters
rescaleFreq           100
rescaleTemp            $temperature

# Periodic Boundary Conditions
cellBasisVector1      60.0  0.0  0.0
cellBasisVector2      0.0  60.0  0.0
cellBasisVector3      0.0  0.0  60.0
cellOrigin             0.0  0.0  0.0
xstFile                z-out.xst
xstFreq               10

```

```

wrapAll          on
wrapNearest      on
wrapWater        on

# Pressure Control
useFlexibleCell   yes

# Berendsen pressure bath coupling
BerendsenPressure      on
BerendsenPressureTarget 1.01325
BerendsenPressureCompressibility 0.0000457
BerendsenPressureRelaxationTime 100

# Interactive Molecular Dynamics
imdFreq      1
imdIgnore    yes
imdOn        yes
imdPort      3111

# script
minimize     100
run          100000

```

This simulation involved a single sodium perfluoro-octanoate molecule placed within a droplet of fifty water molecules. The sodium ion was initially in contact with the perfluoro-octanoate ion, having a geometry similar to the gas phase simulation of sodium perfluoro-octanoate described above. The ion pair was placed in the center of the water droplet. The simulation was maintained at room temperature using temperature rescaling, but periodic boundary conditions were not used.

During the simulation, the perfluoro-octanoate and the sodium ion disassociated and were solvated by the water molecules, which oriented themselves into solvent spheres around the charged ions. The hydrogen and oxygen atoms on the water molecules had the expected orientation relative to the charged species. The perfluoro-octanoate diffused towards the surface of the droplet until the hydrophobic tail extruded from the water droplet. The polar head group remained embedded within the water droplet, solvated by the water molecules.

This simulation was repeated several times with slight modifications to the parameters used and to the initial molecular configuration. In all cases the above results were obtained after a relatively short amount of simulation time. This qualitative accuracy and reproducibility gives us confidence in the quality of the simulation parameters. With further refinements we might expect to obtain quantitative information in good agreement with experimental measurements. Quantities such as solvation energies of the sodium perfluoro-octanoate could potentially be obtained, although much larger water droplets would likely be necessary for accurate determination.

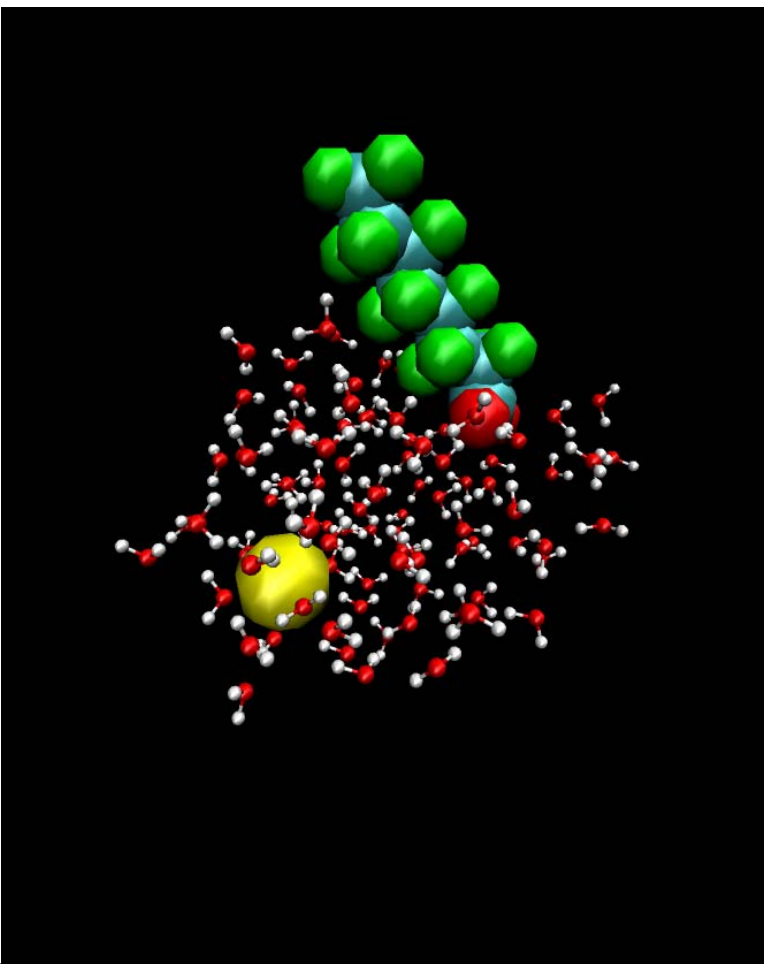
### Surfactant Molecule in Liquid Media.

This simulation involved a single sodium perfluoro-octanoate molecule placed within a droplet of fifty water molecules. The sodium ion was initially in contact with the perfluoro-octanoate ion, having a geometry similar to the gas phase simulation of sodium perfluoro-octanoate described above. The ion pair was placed in the center of the water droplet. The simulation was maintained at room temperature using temperature rescaling, but periodic boundary conditions were not used.

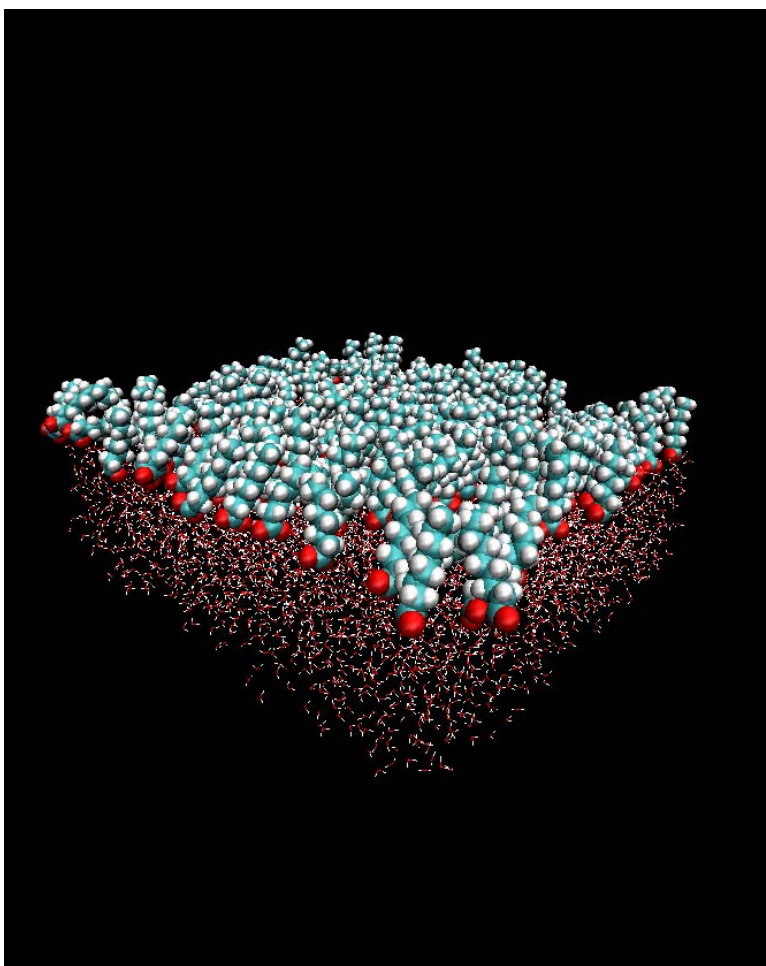
During the simulation, the perfluoro-octanoate and the sodium ion disassociated and were solvated by the water molecules, which oriented themselves into solvent

spheres around the charged ions. The hydrogen and oxygen atoms on the water molecules had the expected orientation relative to the charged species. The perfluoro-octanoate diffused towards the surface of the droplet until the hydrophobic tail extruded from the water droplet. The polar head group remained embedded within the water droplet, solvated by the water molecules.

This simulation was repeated several times with slight modifications to the parameters used and to the initial molecular configuration. In all cases the above results were obtained after a relatively short amount of simulation time. This qualitative accuracy and reproducibility gives us confidence in the quality of the simulation parameters. With further refinements we might expect to obtain quantitative information in good agreement with experimental measurements. Quantities such as solvation energies of the sodium perfluoro-octanoate could potentially be obtained, although much larger water droplets would likely be necessary for accurate determination.



**Figure 24: A simulation of sodium PFOA solvated by a water droplet.**



**Figure 25: A simulation of a partial layer of octanoic acid molecules at an air/water surface.**

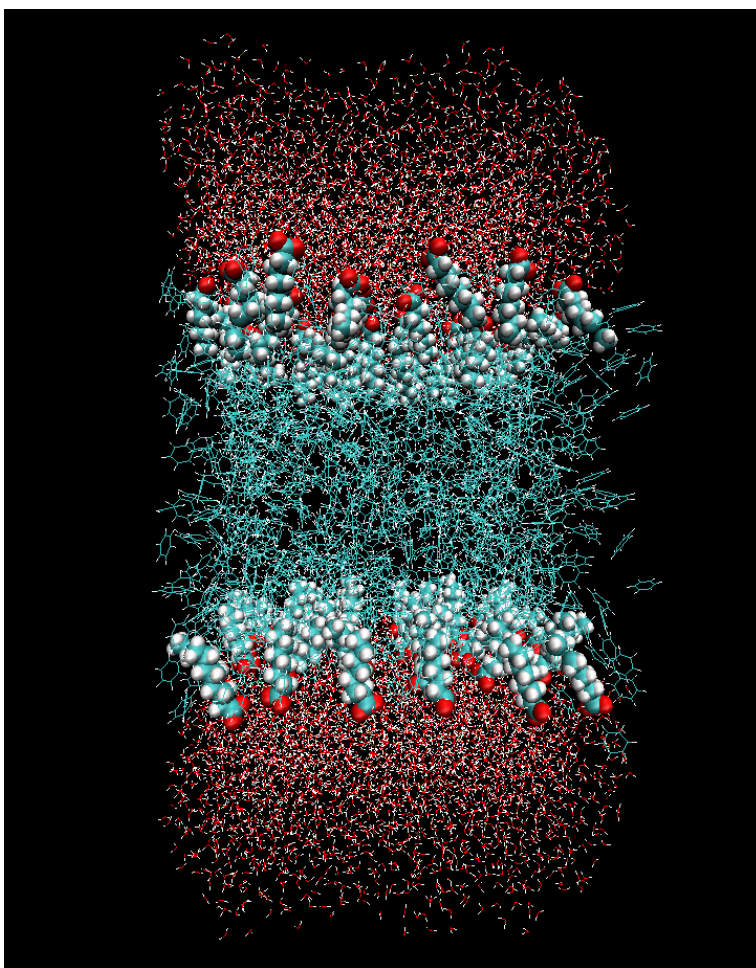
### **Surfactant Layer at a Air/Water Interface.**

This simulation involved modeling sixty-four octanoate ions at the surface of a layer of water. This could be described as an air/water interface, although no nitrogen or other atmospheric gasses were explicitly included in the simulation. The simulation maintained the system at room temperature using temperature recalling, and utilized periodic boundary conditions with a square unit cell of constant size. Therefore the system modeled a thin, infinite sheet of water covered by a layer of sodium octanoate ions.

During the simulation, the octanoate ions remained at the air/water interface, with their hydrophilic head groups solvated by water molecules and their

hydrophobic tails extending into the air.

The surface in this particular case was not saturated by octanoate ions. When viewed from the top there appeared to be approximately fifty percent coverage of the surface. Repeating this simulation with differing numbers of octanoate ions would permit a number of properties to be estimated, such as the area per molecule at saturation. Ultimately we expect to obtain physical properties such as surface pressures and surface diffusion rates from similar simulations.



**Figure 26: A simulation of octanoic acid molecules at benzene/water interfaces.**

### **Surfactant Layer at a Fuel/Water Interface.**

This simulation modeled alternating layers of water and benzene, with octanoate ions placed at each benzene/water interface. The system was maintained at room temperature and pressure using the appropriate methods. Periodic boundary conditions were utilized, with a rectangular, flexible unit cell reproduced infinitely along each dimension. Each unit cell included two benzene/water interfaces, with thirty two octanoate ions at interface for a total of sixty four molecules per unit cell.

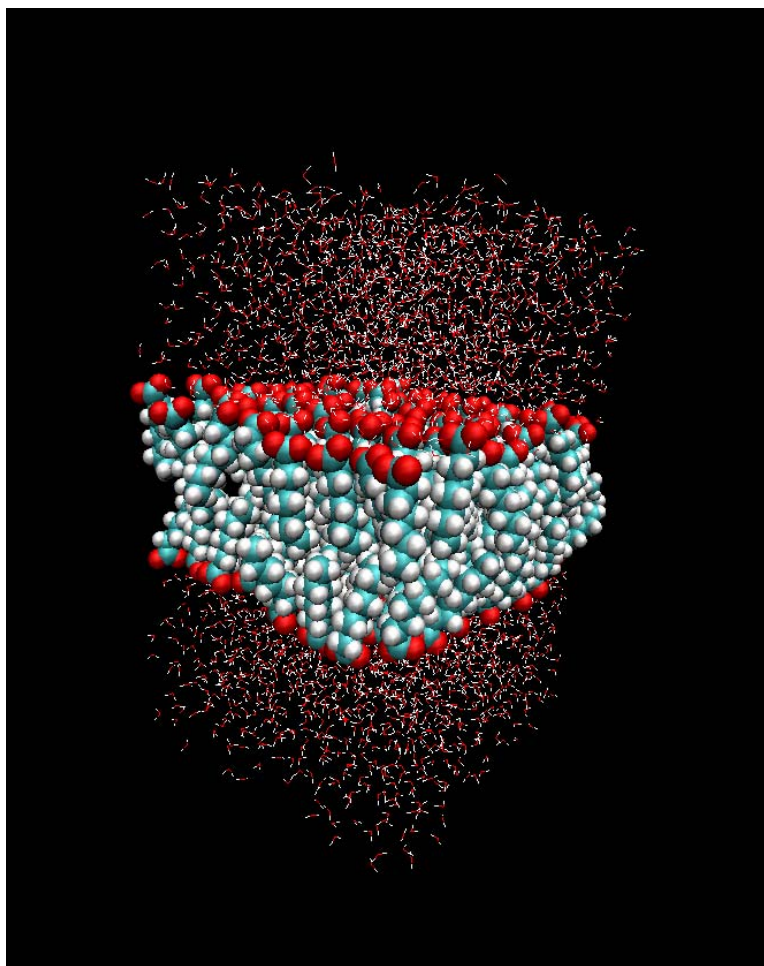
During the simulation, the octanoate ions remained at the benzene/water interface, with their hydrophilic head solvated by water molecules and the hydrophobic tail extending into the organic

benzene layer.

This simulation is complimentary to the one described above. Interfacial properties such as area per molecule, diffusion rates, and interface pressures, may again be considered. Understanding the behavior of fire fighting agents in these two environments may lead to an understanding of why certain agents exhibit superior performance.

### Surfactant Bi-Layer in Water.

This simulation consisted of a bilayer of octanoate ions in water. The system was maintained at room temperature and pressure using the appropriate methods. Periodic boundary conditions were utilized, with a rectangular, flexible unit cell reproduced infinitely along each dimension. Each unit cell consisted of two layers of sixty four surfactant molecules, for a total of one hundred twenty eight surfactant molecules. Each layer of sixty four surfactant molecules was initially placed such that their head groups were in contact with the water layer and their hydrophilic tails were in contact with the adjacent octanoate layer. The octanoate ions were oriented so that they were perpendicular to the octanoate layer. Surfactant molecules were packed in close proximity to each other and the cell size was chosen so that the interface appeared to be saturated with surfactant molecules.



**Figure 27: A simulation of a bilayer of octanoic acid molecules in water.**

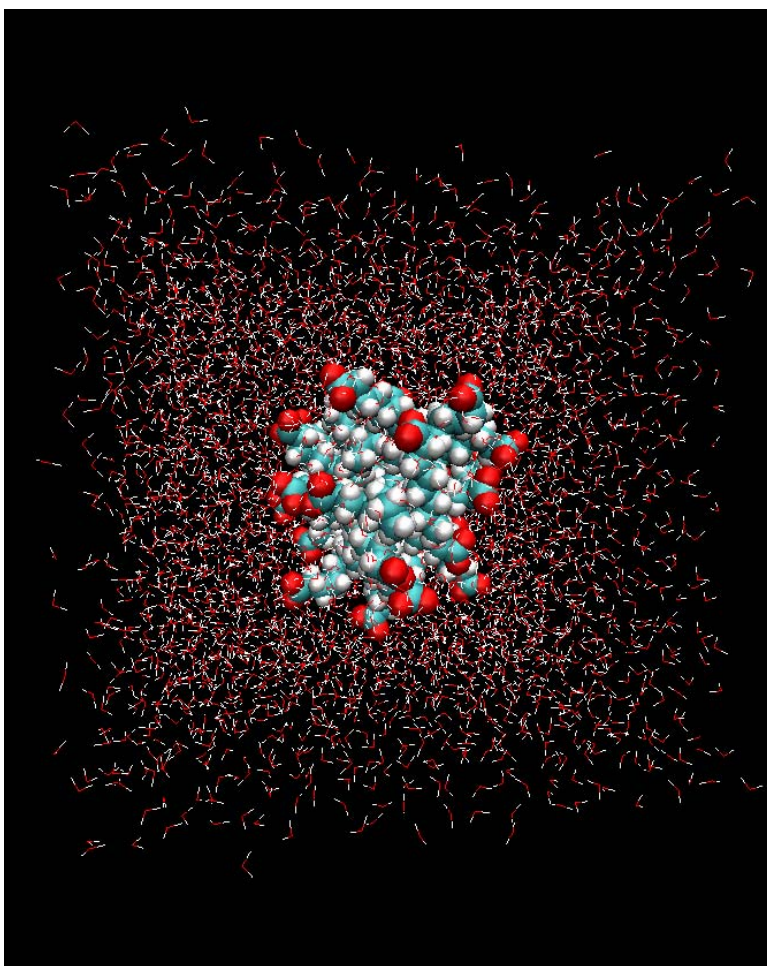
During the course of the simulation, a significant rearrangement of surfactant molecules occurred. The unit cell gradually compacted along the axis perpendicular to the bi-layer (the Z axis) and expanded along the plane of the bi-layer (the X and Y axis). This resulted in the bi-layer being compressed. The surfactant molecules remained approximately linear, but tilted so that they were no longer perpendicular to the bi-layer.

This arrangement of molecules simulated a portion of a macroscopic structure that can be formed by many surfactant molecules at high concentrations in aqueous environments. We do not know if the sodium octanoate would form such structures, but the methods used to set up and model this simulation can be applied to any molecule of interest. In this simulation, we believe we were able to reproduce the proper orientation and geometric conformation that this surfactant molecule would adopt in a saturated bi-layer structure under these physical conditions. Ultimately, we intend to obtain kinetic information about this system such as the diffusion rate of surfactant molecules along the

bi-layer and thermodynamic information about the energies of formation of such macrostructures.

### **Surfactant Micelle in Water.**

This simulation consisted of a cluster of octanoate ions in water. The system was maintained at room temperature and pressure using the appropriate methods. Periodic boundary conditions were utilized, with a rectangular, flexible unit cell reproduced infinitely along each dimension. Each unit cell consisted of a cluster of twenty surfactant molecules. The octanoate ions were initially oriented in a symmetric, approximately spherical pattern, with their hydrophobic tails oriented towards the interior of the cluster and their hydrophilic head groups pointed towards the surrounding water.



**Figure 28: A simulation of a cluster of octanoic acid molecules in water.**

During the simulation, the octanoate ions were seen to deviate from their initial placement and move within the cluster. The cluster as a whole lost its near spherical symmetry and adopted a disorganized, unsymmetrical geometry. However, no octanoate ions left the cluster and diffused into the surrounding water during the course of the simulation. Also, the hydrophobic head groups remained oriented towards and solvated by, the surrounding water.

This simulation was intended to simulate a small cluster, or micelle type structure, that surfactant molecules are known to adopt in aqueous media. Micelle formation is a very important phenomenon and explains many of the important properties of surfactants such as their ability to solvate

hydrophobic compounds in an aqueous solution. By simulating clusters of differing sizes for long simulation times we intend to determine micelle formation constants and critical micelle constants (CMCs) for surfactant species of interest.

## EXPERIMENTAL METHODS AND PROCEDURES.

### Agent Interfacial Tension.

Dynamic Interfacial Tension data between a variety of Mil-Spec AFFFs and simulated fuels were determined using the Kruss Drop Volume Tensiometer, DVT 30. Various experimental conditions were initially used in order to determine an appropriate testing method. Ansul AFFF was selected as a benchmark material to use to determine operating conditions for the instrument. Measurements will be made with three different hydrocarbon liquids, tetradecane, cyclohexane, and xylenes, as these materials represent different sets of fluids found in jet fuel. Tetradecane is useful because it is the easiest of the three to do computer models of, and measurements with this compound might provide feedback to the modeling parameters.



**Figure 29: The Kruss Drop Volume Tensiometer**

The Kruss DVT30 is capable of operating in three modes:

- Interfacial Tension (IFT), Falling Drop
- IFT, Ascending Drop
- Surface Tension

Because of the complexity of the systems being investigated, work is expected to be performed using all three methods to determine either if one is superior or if each in its own way contributes to the understanding of the interactions. At this stage of the investigation, the falling drop method appears to have the advantage of being easier to clean and thus reduce carryover effects from the previous surfactant. This is due to the fact that changing from one surfactant to another involves cleaning a syringe, whereas in the ascending drop method, the entire cell must be removed and thoroughly cleaned.

This report describes work using the first two techniques. It is anticipated that surface tension work will be done later in the course of this study.

The portion of the work described below pertaining to Falling Drop studies in cyclohexane and tetradecane, and Ascending Drop studies involving Ansul AFFF were performed by U.S. Air Force Captain Gina Canfield while on assignment to MLQD as part of her Air Force Reserve Duty. Captain Canfield also contributed significantly to the determination of CMC values using surface tension measurements as described in B. of this section. Captain Canfield is also responsible for writing the operating instructions for the Kruss DVT30.

## **Falling Drop**

### Cyclohexane

Concentrated Ansul AFFF for 3% proportioning was used to prepare 0.3%, 1.0% and 3.0% solutions. The interfacial tension between each of these solutions and cyclohexane was determined using the tensiometer's falling drop method. In this method, the capillary was positioned at the top of the cell, which was filled with the less dense cyclohexane. Drops of the denser Ansul AFFF were flowed from the syringe through the capillary to the bottom of the cell starting at a flow rate of 100  $\mu\text{mL}/\text{min}$  and ending at a flow rate of 0.05  $\mu\text{L}/\text{min}$ . The instrument was programmed to complete 5 flow rate cycles per decade and 5 drops per cycle with a cycle termination of 3 drops if the standard deviation between interfacial tension measurements was 0.1 mN/m or less.

In order to see more of an earlier interfacial change earlier in time, a syringe speed of 500  $\mu\text{L}/\text{min}$  was used. To enhance the detail of the method, the instrument program was changed to increase the number of flow cycle rate from 5 to 20 per decade.

### Tetradecane

Interfacial tension experiments continued using only 3.0% AFFF and a new simulated fuel, tetradecane. The instrument was once again set up for falling drop measurements and the program was initially the same as for the previous tests, however; during the

experiment, the starting flow rate for the last three runs was increased to 500  $\mu\text{L}/\text{min}$ . This was done in order to see more of an interfacial tension change earlier in time.

## **Ascending Drop**

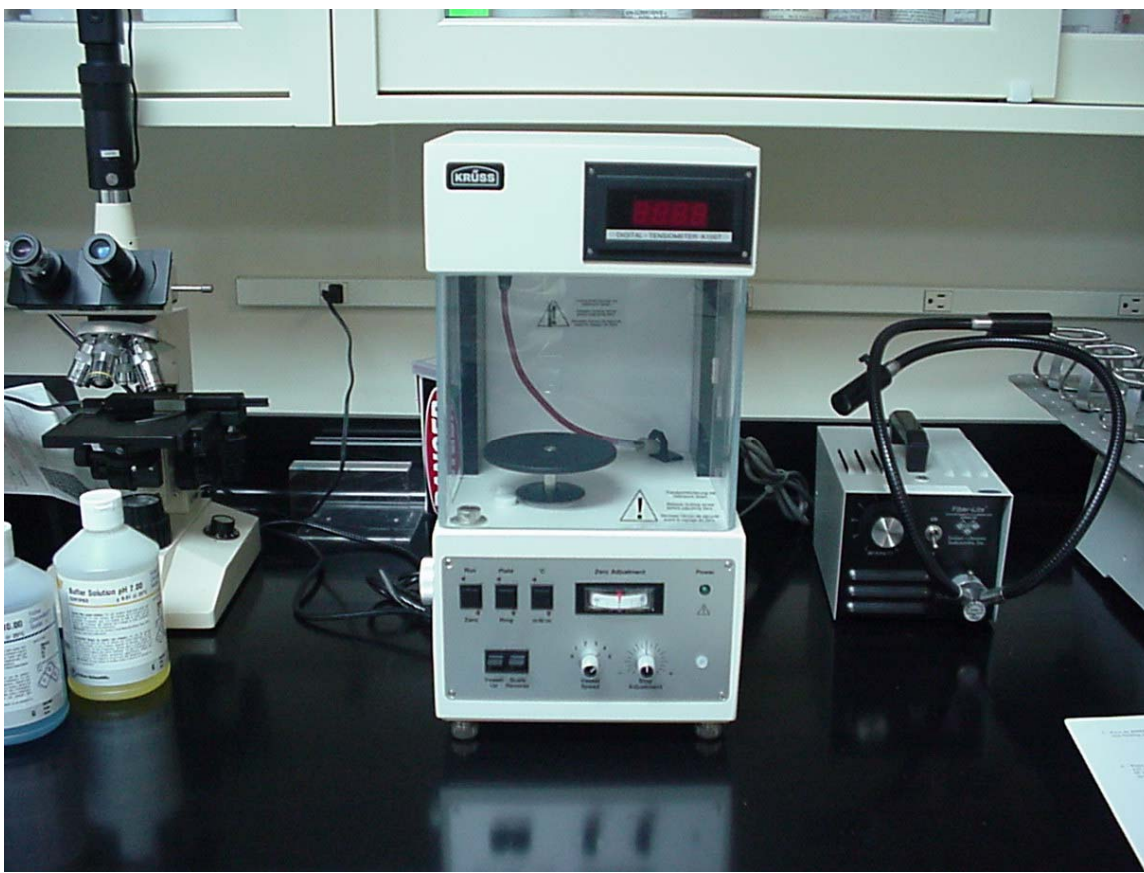
### Tetradecane

Initially, the dynamic interfacial tension between 3.0% AFFF and tetradecane was determined using the ascending drop method. In this method, the capillary was positioned at the bottom of the cell, which was filled with AFFF. Drops of tetradecane were then flowed through the capillary to the top of the cell starting at a flow rate of 500  $\mu\text{L}/\text{min}$  and ending at a flow rate of 0.05  $\mu\text{L}/\text{min}$ . Once again, the instrument was programmed to complete 5 flow cycles per decade and 5 drops per cycle with a termination of 3 drops for standard deviations within 0.1 mN/m.

Additional work was performed with Ansul and four other AFFFs (National Foam, 3M, Tridol M, and Aer-O-Water), all at the 3% dilution from 3% concentrate. The purpose was to observe any differences in the curves obtained and at a later date to see if there is a correlation between these differences and the actual performance of these agents in a Mil-Spec test. Testing conditions were modified to a starting flow rate of 300  $\mu\text{L}/\text{min}$  and ending at no slower than 1  $\mu\text{L}/\text{min}$ . These changes were made as it was observed the faster syringe speed was too fast for the instrument to give reliable results. As it was decided that the region of greatest interest was in the earliest stages of surface age, the sampling was increased from 5 to 20 flow cycles per decade.

### Surfactant Surface Tension

With the appropriate interfacial tension testing methods determined, measurements of individual surfactants were then needed. The recommended concentrations or the critical micelle concentrations, CMC, were first determined. Solutions of sodium octanoate (NO), sodium decanoate (ND), and sodium perfluoro-octanoate (NPFO) were prepared from their acids at their highest possible concentrations then serially diluted by factors of 10. For sodium perfluoro decanoate (NPDF), due to the relative insolubility of its sodium salt, it was not possible to prepare a solution at high enough concentrations to have sufficient data to determine the CMC. At a later date an attempt will be made to determine the values for another salt, either lithium or ammonium. The equilibrium surface tension for each solution was then measured in a 250 mL beaker with a platinum/iridium Wilhelmy plate using a Kruss Digital Tensiometer, K10ST. The CMC was determined using a graph of surface tension vs. concentration. These studies were initiated by Capt. Canfield and continued by Seymour Stern.



**Figure 30: The Krüss Digital Tensiometer.**

### **Surfactant Interfacial Tension**

Dynamic interfacial tension measurements between individual surfactants and various hydrocarbon liquids were then determined. Solutions of each of the surfactants just above their CMC were prepared and used to fill the cell of the Krüss Tensiometer in either an ascending or descending drop format. The syringe, filled with appropriate material, was set for an initial flow rate of 300  $\mu\text{L}/\text{min}$  and a terminal flow rate of 1  $\mu\text{L}/\text{min}$ .

### **Ascending Drop**

#### **Tetradecane**

Sodium octanoate (NO), sodium decanoate (ND), sodium perfluoro octanoate (NPFO), sodium perfluoro decanoate (NPFD) were prepared from their organic acids to form the salts. For NPFO the solution was made basic with an excess of sodium hydroxide. Measurements were done with these materials. Additionally a combination of NPFO and NO were analyzed to see if the combination could replicate Ansul AFFF.

Two commercial surfactants, Triton X45 and Triton X165, each containing slightly different formulations of ethoxylated alkyl phenol were tested at slightly above their respective CMC values. CMC values were provided by the supplier.

Cyclohexane.

Complimentary studies of the above materials were performed with cyclohexane.

**Falling Drop.**

Samples run in ascending drop were also analyzed by descending drop for tetradecane and cyclohexane.

**Surfactant Surface pressure.**

Using a NIMA Langmuir Blodgett trough it is intended to determine surface pressure vs. area isotherms. From these isotherms surface area/molecule data will be derived. This data will be used to verify the accuracy of computer modeling experiments.

The two dimensional miscibility of surfactant mixtures can also be evaluated.<sup>20</sup>

**Agent Surface Pressure.**

It is anticipated that the NIMA Langmuir Blodgett trough will be used on agents as well individual surfactants.

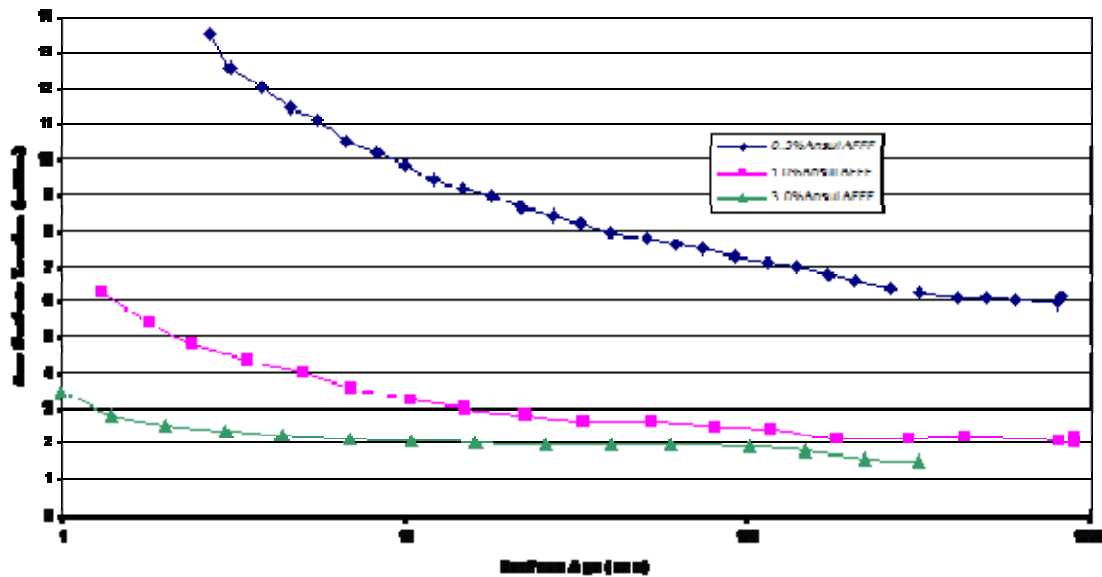
**EXPERIMENTAL RESULTS.**

**Agent Interfacial Tension.**

**Falling Drop.**

Cyclohexane.

The first sets of dynamic interfacial tension data collected were between Ansul AFFF and cyclohexane using the falling drop method.

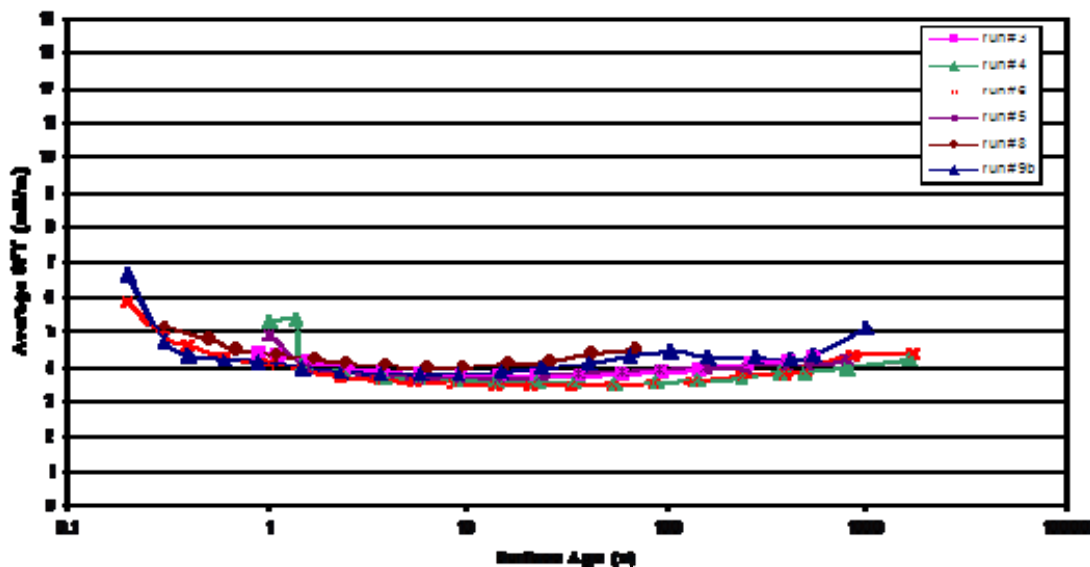


**Figure 31: Ansol AFFF and Cyclohexane Interfacial Tension.**

This data helped verify the physical differences between different concentrations. As expected, the interfacial tension between AFFF and cyclohexane decreases as the AFFF concentration increases. For the recommended concentration of AFFF, 3.0%, the system comes to equilibrium in 10 seconds and the interfacial tension has decreased to 2.0 mN/m.

#### Tetradecane

For comparison, this experiment was repeated for tetradecane as the simulated fuel with only 3.0% Ansol AFFF as this is the recommended concentration for firefighting.

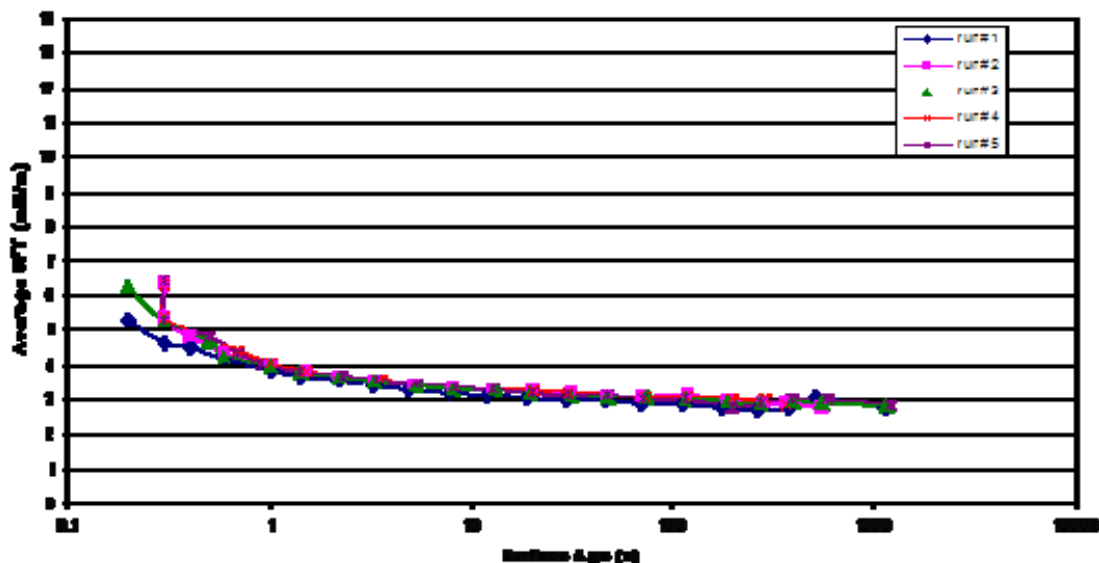


**Figure 32: Ansul AFFF and Tetradecane Interfacial Tension.**

From this data it is evident that 3.0% AFFF reaches equilibrium in approximately one second where the interfacial tension decreases to below 4.0 mN/m.

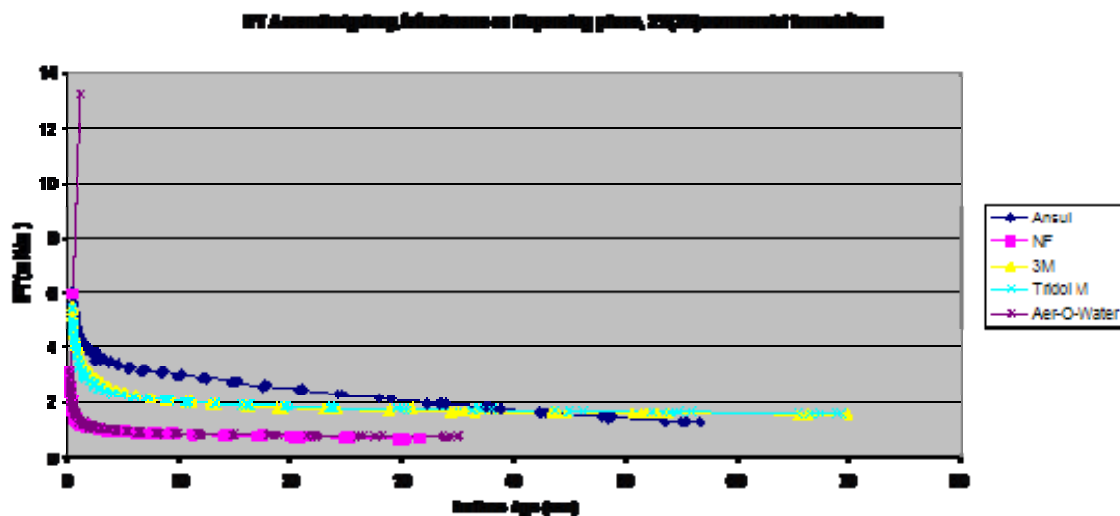
#### **Ascending drop.**

Work was also performed using the ascending drop technique with tetradecane as the dispensing liquid.



**Figure 33: Ansul AFFF and Tetradecane Interfacial Tension, Ascending Drop**

Using the ascending drop method, it is noted that the AFFF/tetradecane system reaches equilibrium at approximately 10 seconds where the interfacial tension has decreased to 3.0 mN/m.

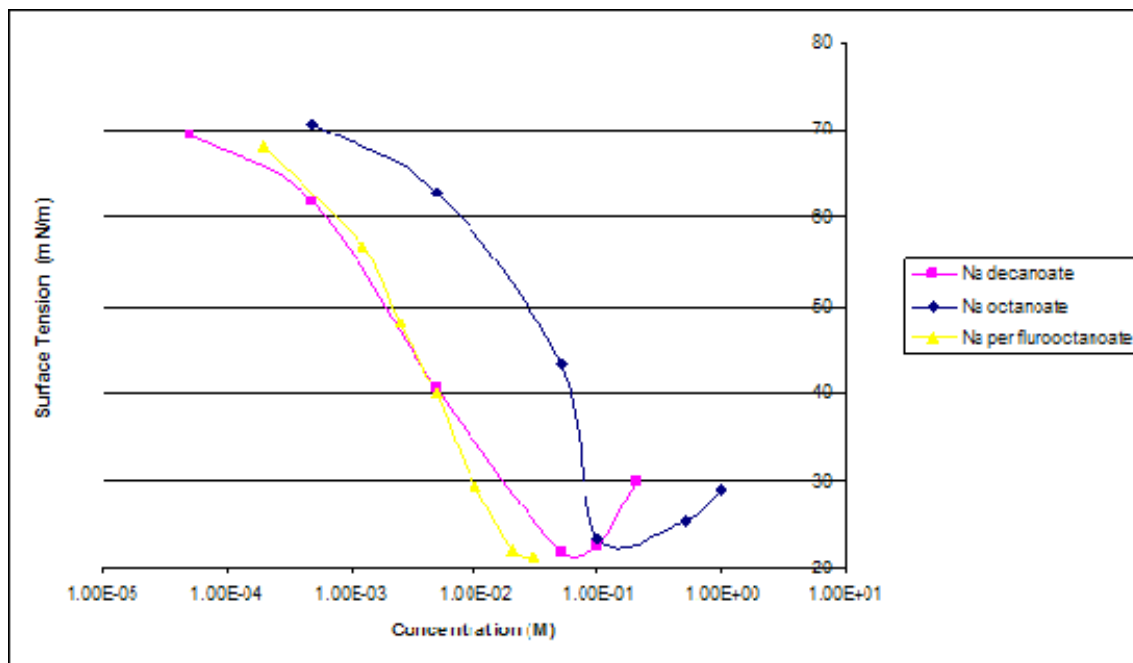


**Figure 34: Mil Spec AFFFs and Tetradecane Interfacial Tension.**

The above chart shows differences in how different commercial formulations come to equilibrium, with different rates and different final values of interfacial tension. The 3M and Tridol M curves are virtually identical to each other, as are the National Foam (NF)

and Aer-O-Water curves. It is not known at this time if there is any correlation between fire fighting performance and these differences.

## Surfactant Surface Tension

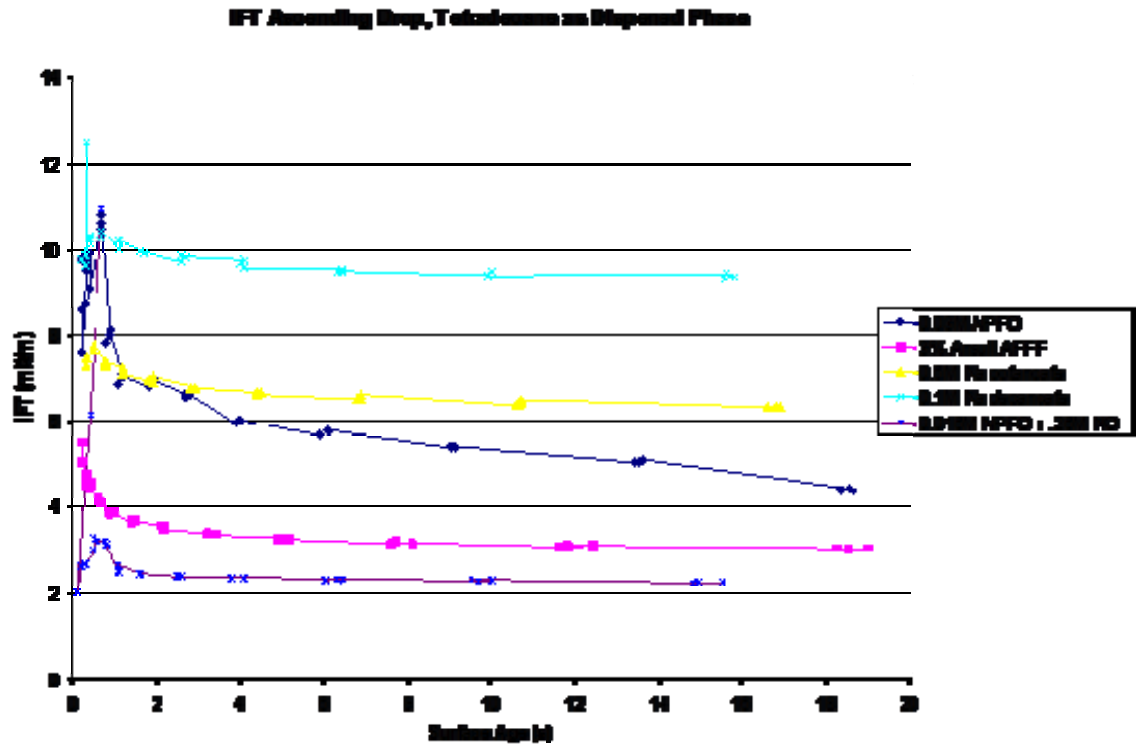


**Figure 35: Surfactant Surface Tension vs. Concentration.**

Figure 5 demonstrates the relationships with increasing concentration of interfacial tensions. The slope change is considered to be the critical micelle concentration (CMC). As mentioned earlier limitations occur when the solubility of the metal salt is below that of the CMC.

## Surfactant Interfacial Tension

### Ascending drop



**Figure 36: Interfacial Tension of Various Surfactants Compared to Ansul.**

The above chart shows two trends. First, the hydrocarbon surfactants near their CMC have relatively higher interfacial tensions than the fluorosurfactants. Also, the rate and time for equilibrium differs significantly. When a fluorosurfactant and hydrocarbon surfactant are combined and measured, the resultant curve combines properties of both, resulting in a curve whose overall shape is similar to that of an Ansul AFFF.

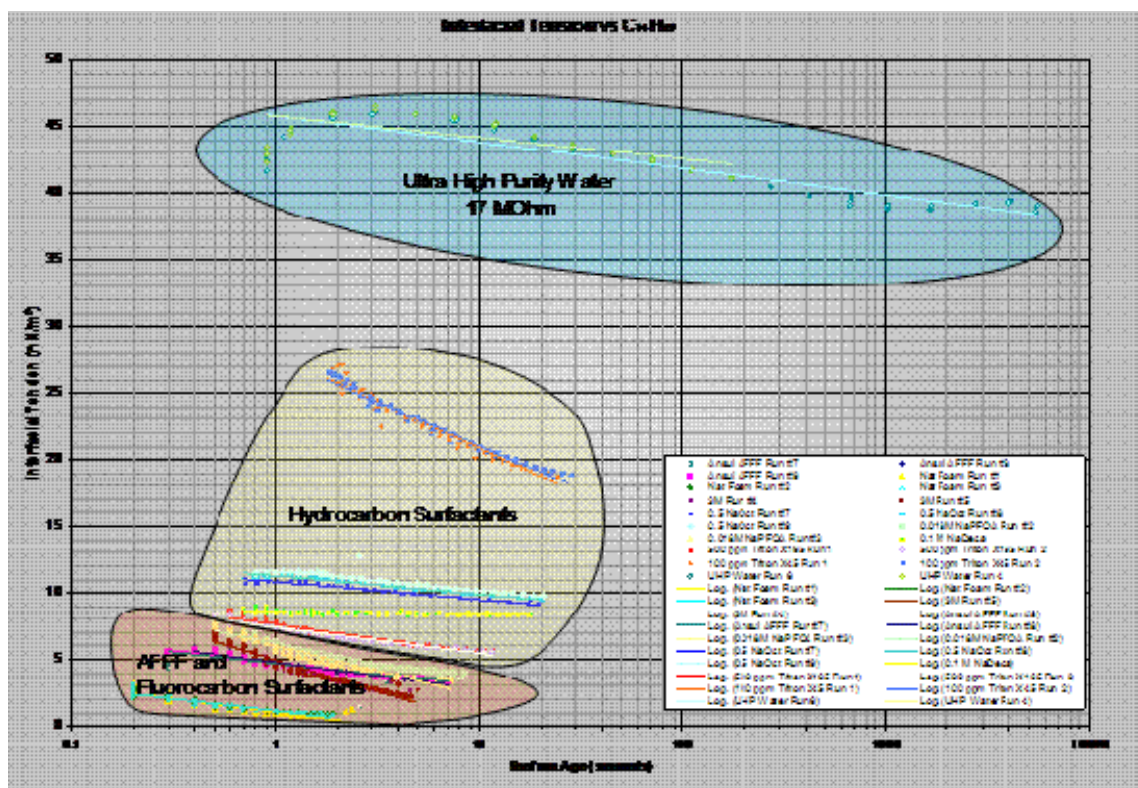


Figure 37: Interfacial Tension of Various Surfactants with Tetradecane.

Figure 7 shows that how a surface agent interacts with a given liquid, in this case tetradecane, will be strongly influenced by the functional groups of the surfactant. It is interesting to observe that fluorocarbon surfactants and AFFF formulations (which contain fluorocarbon surfactants) are in their own region.

## Falling Drop

### Tetradecane

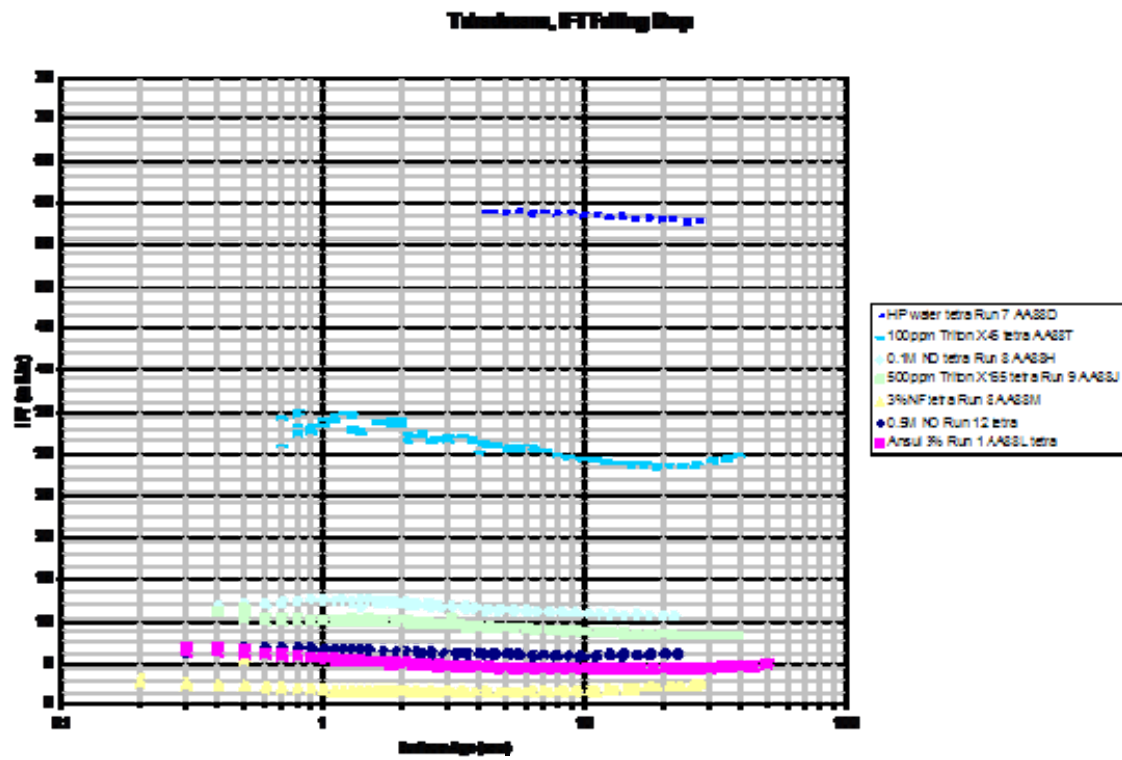
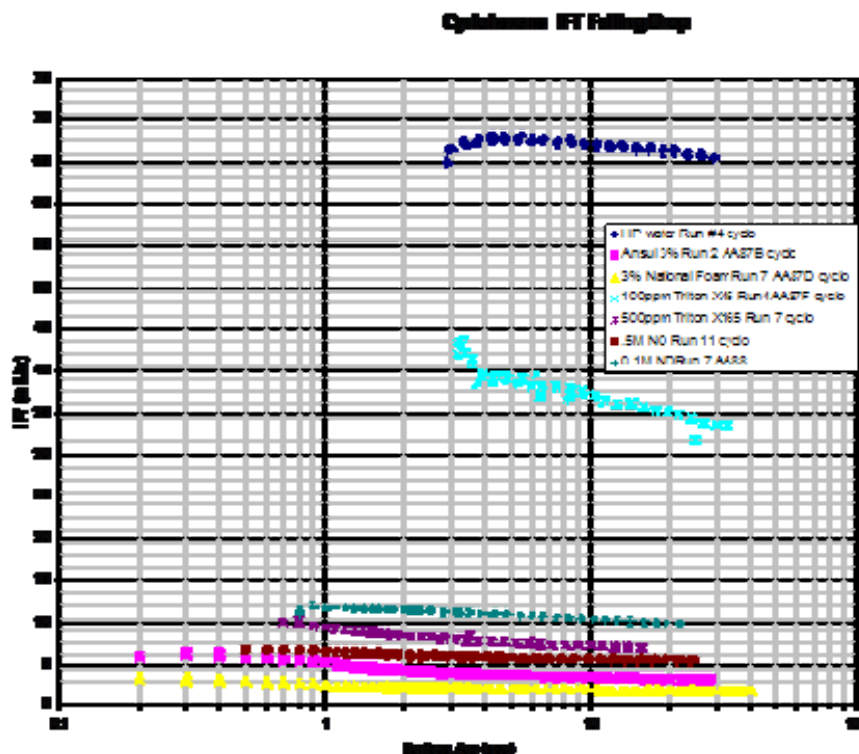


Figure 38: Interfacial Tension of Various Materials in Tetradecane, Falling Drop.

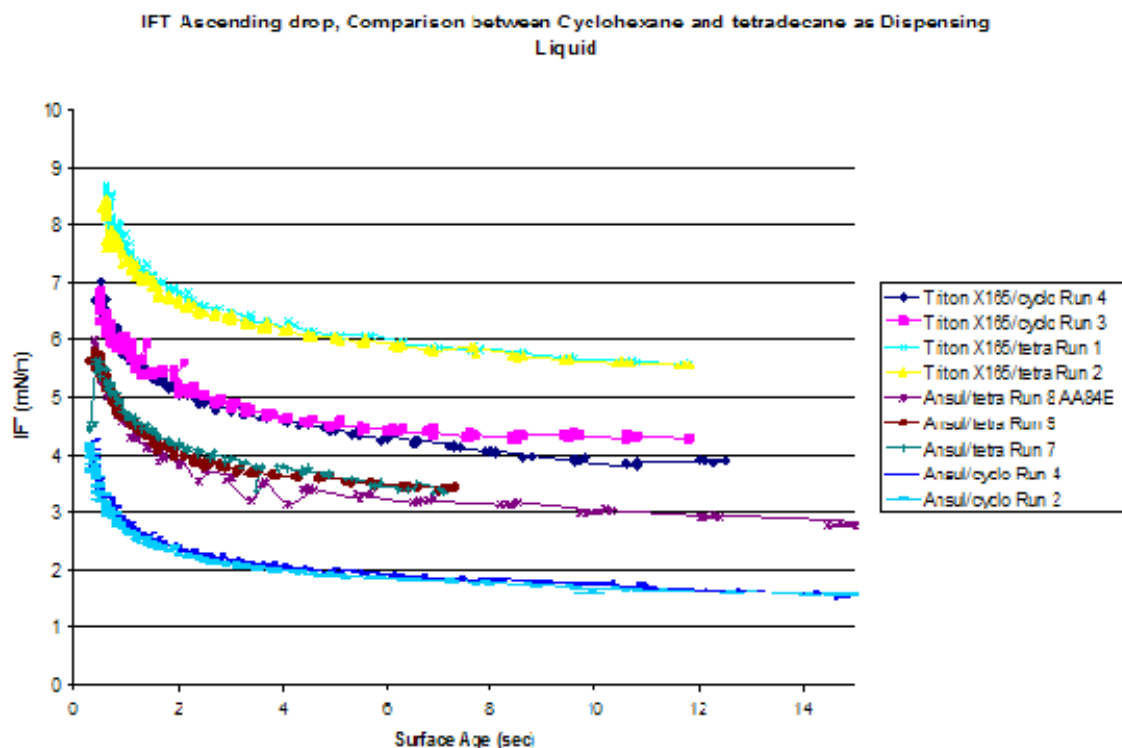
## Cyclohexane



**Figure 39: Interfacial Tension of Various Materials in Cyclohexane, Falling Drop.**

Figures 8 & 9 illustrate the range of surface tensions that different materials exhibit in tetradecane and cyclohexane, respectively, by the falling drop method. In addition to two commercial AFFFs, two commercial surfactants of the Triton X formulation (ethoxylated alkyl phenol), water and two hydrocarbon based surfactants are displayed. While there is some differences in the measured values between the two liquids, the rankings of all materials is the same.

## Cyclohexane vs. Tetradecane Correlation Study



**Figure 40: Interfacial Tension of Various Surfactants in Cyclohexane and Tetradecane.**

Figure 10 shows the differences in interactions between Ansul and Triton X165 to demonstrate that these materials will behave differently depending upon the functional groups that a surfactant is exposed to. It is expected that different surfactants may vary in their relative differences to these fluids. As jet fuel is a mixture of straight chain, cyclic and aromatic hydrocarbons, these differences must be accounted for in both modeling and formulations.

## CONCLUSIONS

Results to date show that:

1. Drop Volume Tensiometry data discriminates between AFFF and AFFF-like *versus* all other tested surfactant systems.
2. Molecular Models can simulate the interfaces required for AFFF modeling.

## RECOMMENDATIONS

1. Conduct further tensiometry studies to further develop kinetic surface tension data.
2. Conduct Langmuir-Blodgett studies to determine surfactant system areas/molecule and two dimensional phase transition data.

3. Continue development of molecular models, and develop predictions of surface tension as a function of surface coverage and area/molecules
4. Prepare a paper for publication in *Langmuir* of these results.
5. Begin modeling of alternative surfactant systems to investigate the types of “tails” which might offer superior performance *visa a vie*

## ACKNOWLEDGEMENTS

The laboratory contributions of Matt Rochefort in determining many interfacial tension values and preparations of many solutions are gratefully acknowledged.

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- 16 **BioSciences Group**, Fujitsu Computer Systems, 200 Lowder Brook Dr. Ste. 2100, Westwood, MA 02090
- 17 **Accelrys, Inc.**, 10188 Telesis Court, Suite 100, San Diego, CA 92121 USA
- 18 NAMD was developed by the Theoretical and Computational Biophysics Group in the Beckman Institute for Advanced Science and Technology at the University of Illinois at Urbana-Champaign."
- James C. Phillips, Rosemary Braun, Wei Wang, James Gumbart, Emad Tajkhorshid, Elizabeth Villa, Christophe Chipot, Robert D. Skeel, Laxmikant Kale, and Klaus Schulten. Scalable molecular dynamics with NAMD. *Journal of Computational Chemistry*, **26**:1781-1802, 2005.  
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## **APPENDIX A: STANDARD OPERATING PROCEDURE FOR KRUSS DVT30 TENSIOMETER.**

### **Software Setup**

Run Kruss software setup on appropriate computer using license number.

Click on the Kruss icon, then the Drop Volume icon.

Go to Tools, then Device Manager.

Click Add; make sure COM-Port is COM 1.

Click Validate Device, and then Apply.

Highlight Use Selected Device.

**\*\*This process is only required the first time the software is setup on a computer.**

### **Instrument Setup**

#### **Bottles, Ports, and Tubing**

The ports and tubing on the left side correspond to the cell. Ports A – D correspond to the red, yellow, green, and blue tubing which connect to sample bottles. Port E (black) connects into the cell. Port F (white) connects to the rinse bottle. **\*Do not use acetone for a rinse solution.\*** Port H (black) connects to the waste bottle.

The ports and tubing on the right side correspond to the syringe. Ports A – D correspond to the red, yellow, green, and blue tubing which connect to sample bottles. Port E connects to the syringe. Port F (white) connects to the rinse bottle. Port G (red) connects to the capillary. Port H (black) connects to the waste bottle.

Fill bottles or flasks with your solutions ensuring that the colored tubing connects to the appropriate inlets, either to the cell or to the syringe.

Using the light phase or ascending drop method, the cell is positioned with the capillary at the bottom. The cell is filled with the more dense solution and the syringe with the less dense solution so that it can be bubbled up.

Using the heavy phase or falling drop method, the cell is positioned with the capillary at the top. The cell is filled with the less dense solution and the syringe with the more dense solution so that it can drop down.

#### **Instrument Display**

On the Main Menu (at any point hit escape to return here) you see cell temperature (within cell) and auxiliary temperature (outside instrument). You will also see F1 as the cell and F2 as the syringe.

Under F1 or F2 you will see options for drain, refill, rinse, and setup. Here you can set the instrument to drain the cell/syringe contents to waste, refill through your chosen port, or rinse with your rinse solution.

Between runs drain the cell and rinse with the rinse solution at least three times. Then open the cell and rinse it down with a rinse bottle to ensure the cell and capillary are clean. (It may be necessary every few runs to remove the capillary and let it soak in ethanol for a few hours.) Close the cell and refill with your sample then drain again, repeat several times to ensure there are no contaminants in the cell.

Between runs drain the syringe and refill with your sample. It should not be necessary to rinse the syringe as it should not be contaminated. If needed the syringe can be rinsed several times, then refilled with sample and drained several times.

When changing liquids in either the cell or syringe, you will need to refill/drain enough times to ensure you've replaced the previous liquid or any air in the lines.

*Ensure that all glassware and bottles used in solution preparation or sampling are thoroughly cleaned with detergent, soaked in acetone, allowed to dry, and rinsed with high purity water before using. Make solutions using the high purity water. Take care not to touch the inside of any glassware or bottles as oils from skin will cause contamination.*

## **Data Acquisition**

Click the Kruss icon on the computer, once the program opens click on the Drop Volume icon.

You will see a tab for Database Explorer that will show you where all your files are stored. You will also see a tab for Project Editor that will allow you to manipulate each file.

For example in the explorer you will see a folder for Demo Measurements, clicking here you will see all the demo runs in that folder and clicking on any one will take you into the editor where you can see the data points and graph. The graphs are displayed as Average Surface Tension vs. Flow Rate or Surface Age.

To start a new data run you must go to File and then New Measurement or to the blank page icon. Here you will see options for IFT (interfacial tension) and SFT (surface tension). Under IFT there are options for Falling Drop and Ascending Drop methods. Under SFT there is only one option for Falling Drop method.

Once you choose your method a box will appear where you will enter your run information and set up your procedure.

Fill in your measurement name and remarks, and then proceed to each tab.

### **Bulk Phase**

Enter the name and density of the component to be added to the cell.

### **Dispensed Phase**

Enter the name and density of the component to be added to the syringe.

\*\* You can browse the database for correct density data.

## **Procedure 1**

**Port Assignment** – Enter the letter of the port to collect sample for the bulk phase (cell) and the dispensed phase (syringe).

**Flow Rate** – Enter the start/stop flow rate. This will be determined for each experiment; however, slower rates should be used for samples with lower surface tensions.

**Acquisition** – Leave this as the default, logarithmic.

**Flows per Decade** – This is the number of measured steps (flow cycles) per interval. Increasing/decreasing this number will increase/decrease the number of points per interval.

**Number of Drops per Cycle** – This is the number of drops to be detected for each flow rate and will also depend on each experiment.

**Capillary Diameter** – 0.2540 mm for IFT and 1.5000 mm for SFT.

**Detection Threshold** – This indicates instrument sensitivity, leave at the default of 5%.

**Correction** – For IFT, the method should be left at none and for SFT the method should be either Harkins/Brown or Rulison.

**Cycle Termination** – This is to set the instrument to stop the flow rate cycle at a certain number of drops if the tension is within a set standard deviation and continue to the next cycle.

## **Procedure 2**

**Syringe Refill Flow Rate** – This is the flow rate for the syringe to refill at if it depletes during an experiment. Leave at the default unless the sample is viscous.

**Cell Flush Time** – This is the delay time for the cell to aspirate off the light phase and is only used for IFT ascending drop and SFT falling drop methods. This can be set at 0 sec after each flow cycle (in order not to flush) and 5-10 sec after measurement.

**Delay between Flow Changes** – This is the delay time between each flow cycle and is usually set for 3 seconds.

**Plots** – This is where you can edit your plot setup.

Once you are ready you can click OK and the new run is filed in a previous or new folder as designated.

Begin the run by clicking Run and then Start Measurement or by clicking the forward arrow icon.

Stop the run by clicking Run and then Stop Measurement or by clicking the square icon.

Data is saved here or it can be copied into Excel.

For a new measurement, this process can simply be repeated.

## **Theory**

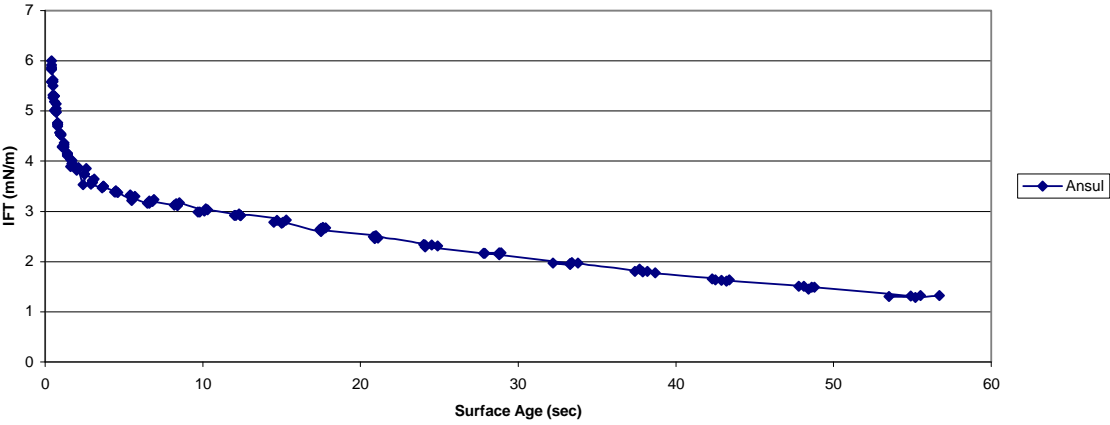
Because water has a dipole it exhibits the intermolecular force of Hydrogen Bonding and the molecules will align themselves to maximize this force. A molecule in the bulk phase is surrounded by other molecules and therefore attracted in all directions equally. However, a molecule on the surface is not completely surrounded. There are no forces pulling on it from above, this force imbalance causes the molecules to be pulled inward which is what causes surface tension.

The free energy at the water surface is positive which means the surface tension – the work required to expand the surface – is high. When a surfactant molecule enters, it disorients the water structure as the water moves from the hydrophobic chain. Then the surfactant will orient itself with its chain directed out of the water. This causes an increase in the entropy and a decrease in the free energy, which means the surface tension – the work needed to move the surfactant to the surface – is decreased. This allows more surfactant molecules to accumulate at the surface, which will further decrease the surface tension. So the surface tension should decrease over time.

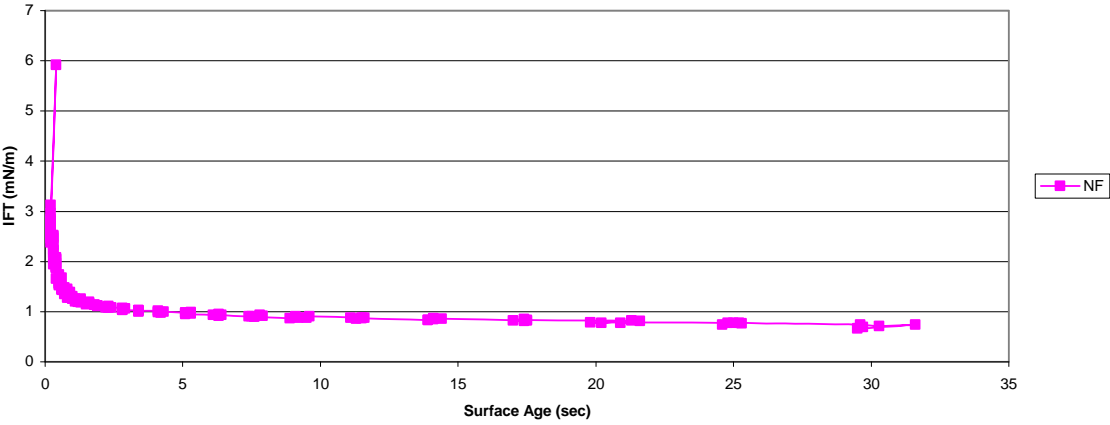
In this instrument a droplet of liquid enters another liquid through a capillary. Based on their interfacial tension, this droplet will split into more and more smaller droplets over time. The more small droplets formed, the lower the interfacial tension and the fewer large droplets formed, the higher the interfacial tension. To see this, the instrument will vary the flow rate of the first liquid into the second. At a slow flow rate the droplet will have more time to split and create more small droplets indicating a low tension. As the flow rate increases the droplet has less and less time to split creating fewer large droplets and indicating an increasingly higher tension. So you see the tension increase with flow rate, which translates into a decrease in tension over time. The instrument has an LED to detect these drops and will calculate their volume and then the interfacial tension.

**APPENDIX B: ADDITIONAL EXPERIMENTAL DATA**

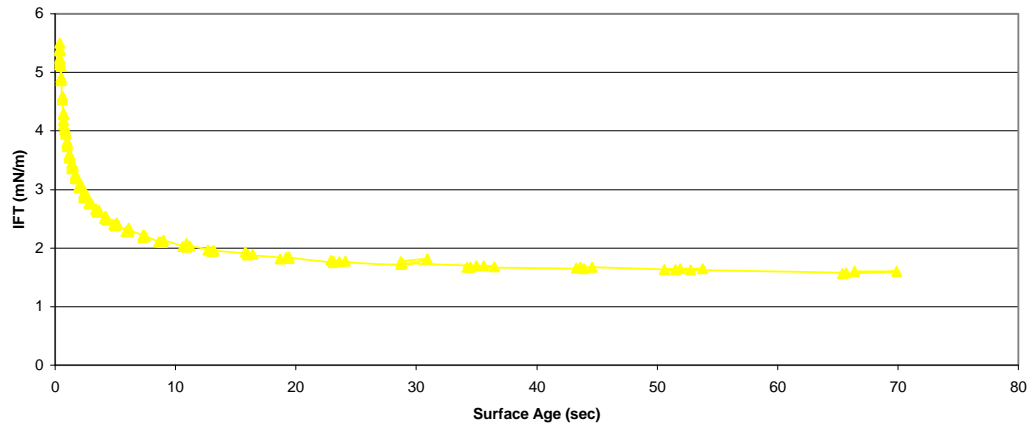
**IFT Ascending drop, tetradecane as dispensing phase,  
3%(3%) commercial formulations**



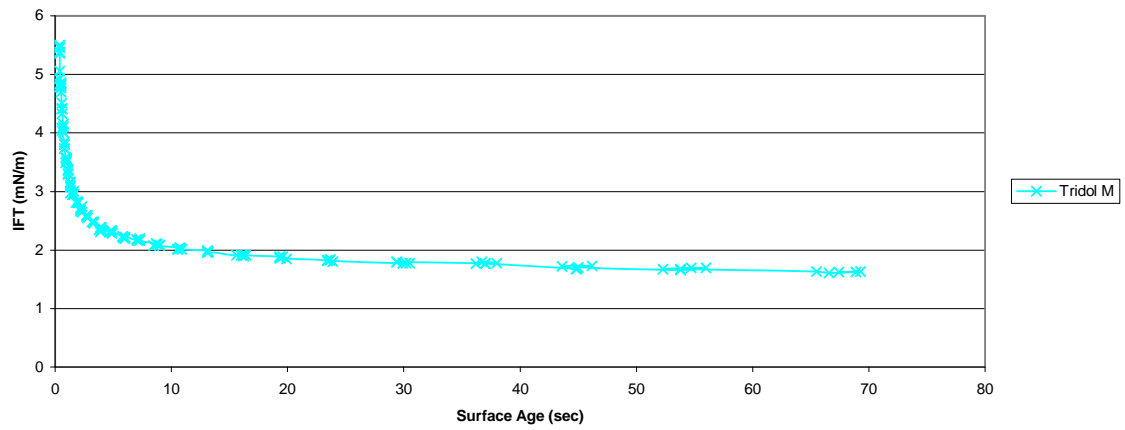
**IFT Ascending drop, tetradecane as dispensing phase,  
3%(3%) commercial formulations**



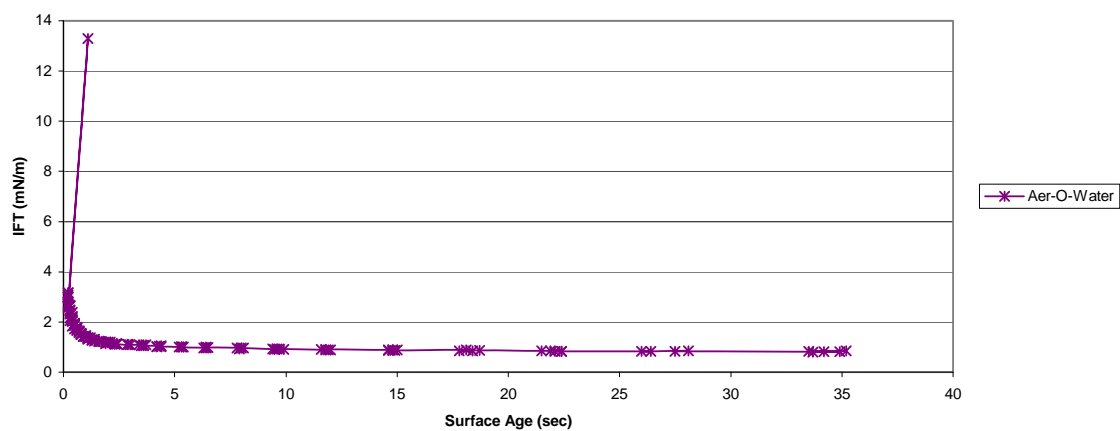
IFT Ascending drop, tetradecane as dispensing phase,  
3%(3%) commercial formulations



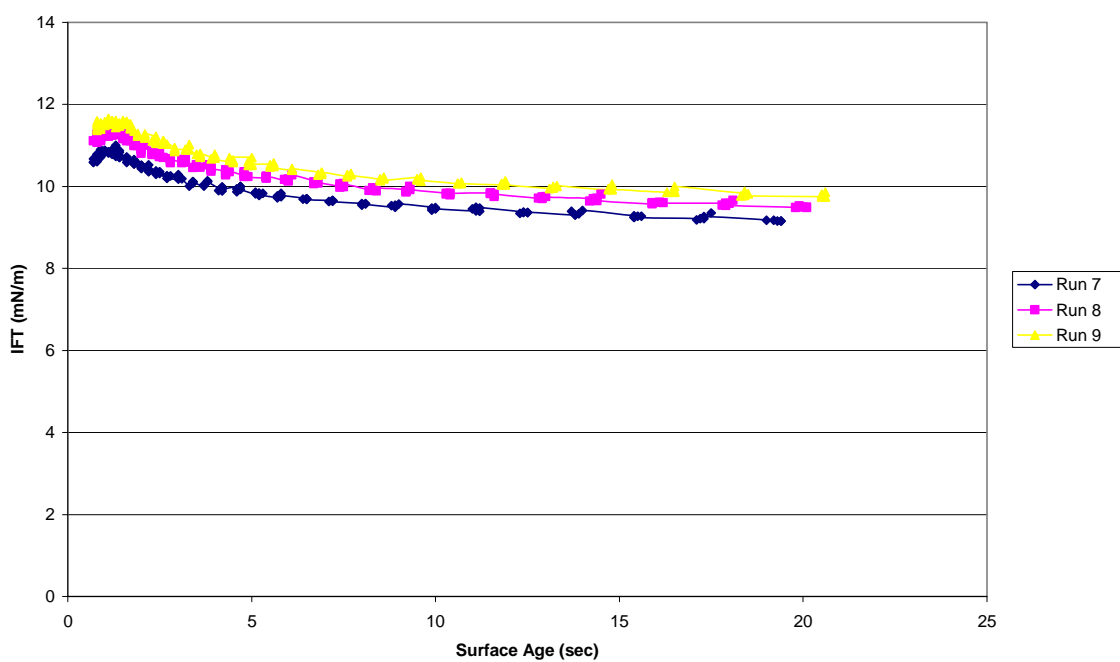
IFT Ascending drop, tetradecane as dispensing phase,  
3%(3%) commercial formulations



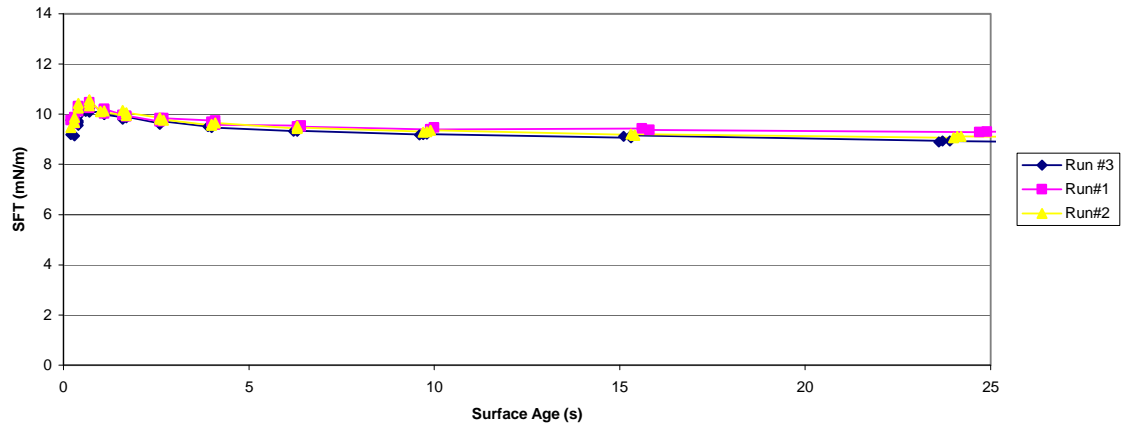
IFT Ascending drop, tetradecane as dispensing phase,  
3%(3%) commercial formulations



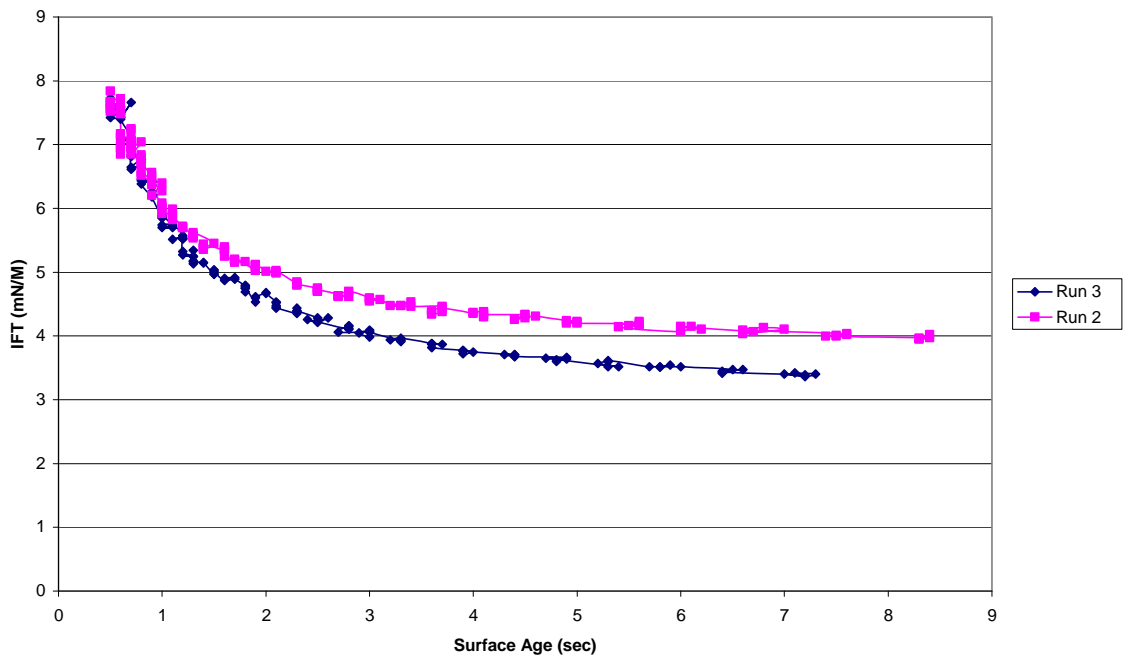
IFT Ascending Drop Tetradecane vs.  
0.5 M Sodium Octanoate



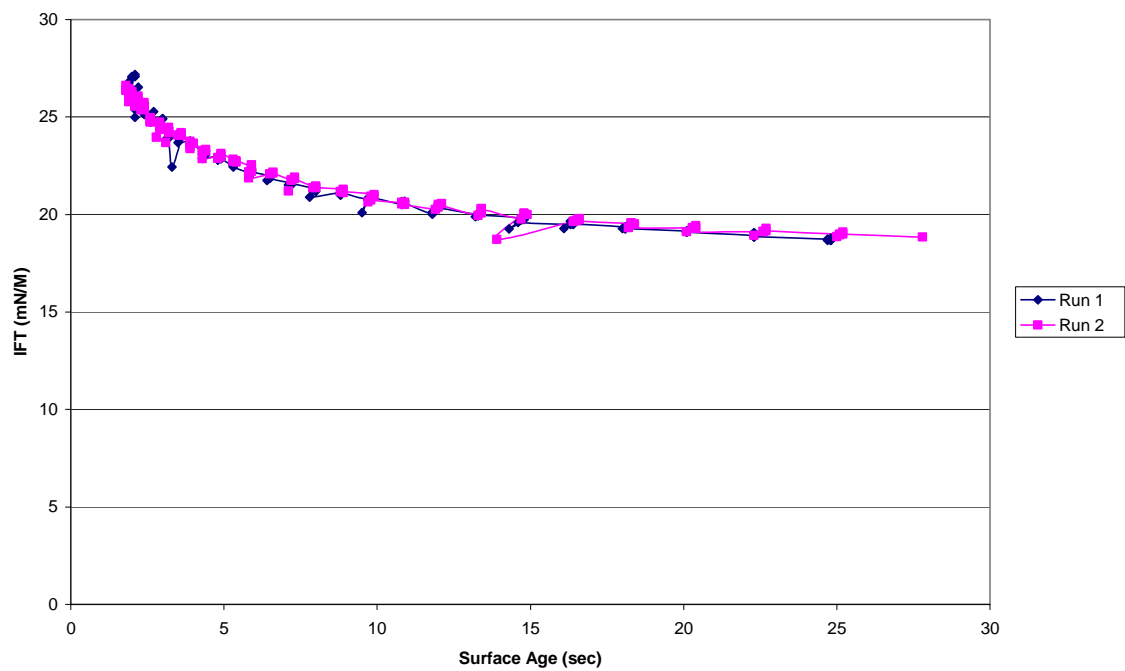
IFT Ascending Drop, Tetradecane vs.  
0.1 M Sodium decanoate



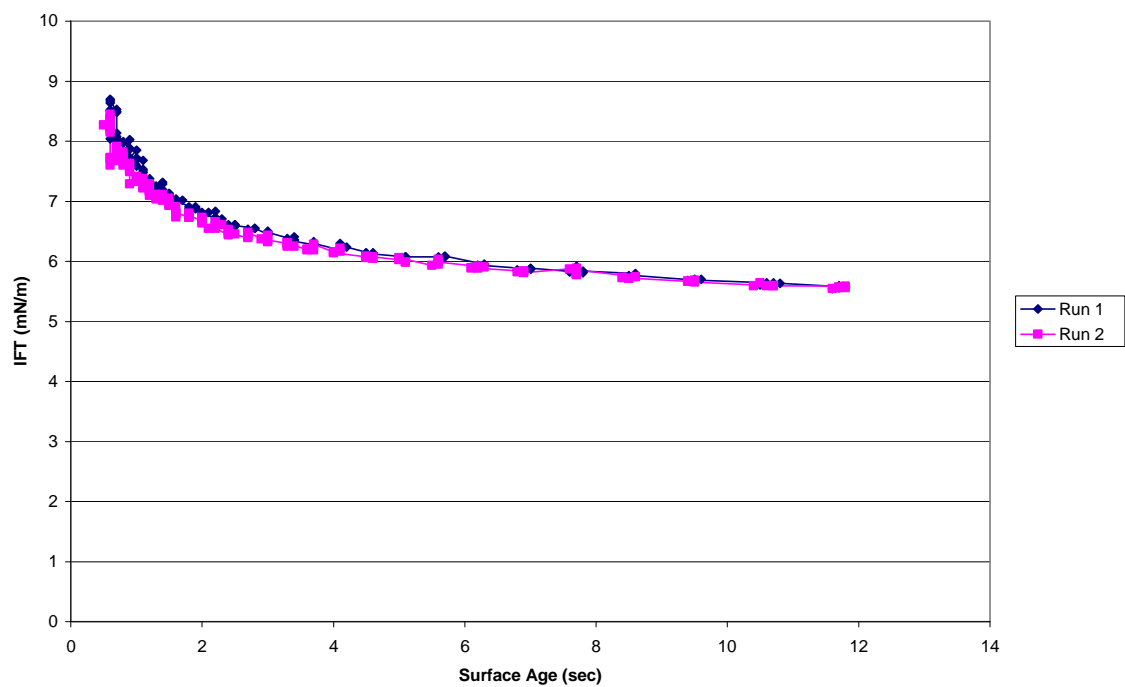
IFT Ascending Drop, Tetradecane vs.  
0.18M Sodium perfluoro octanoate



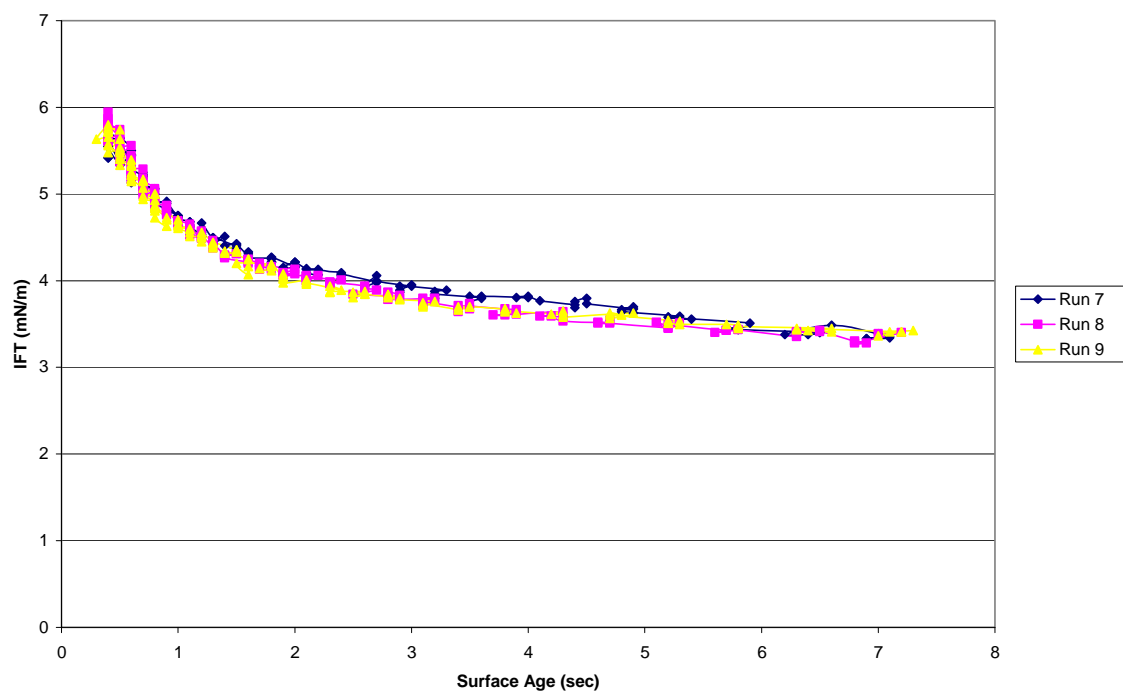
IFT Ascending Drop, Tetradecane  
vs. 100ppm Triton X45



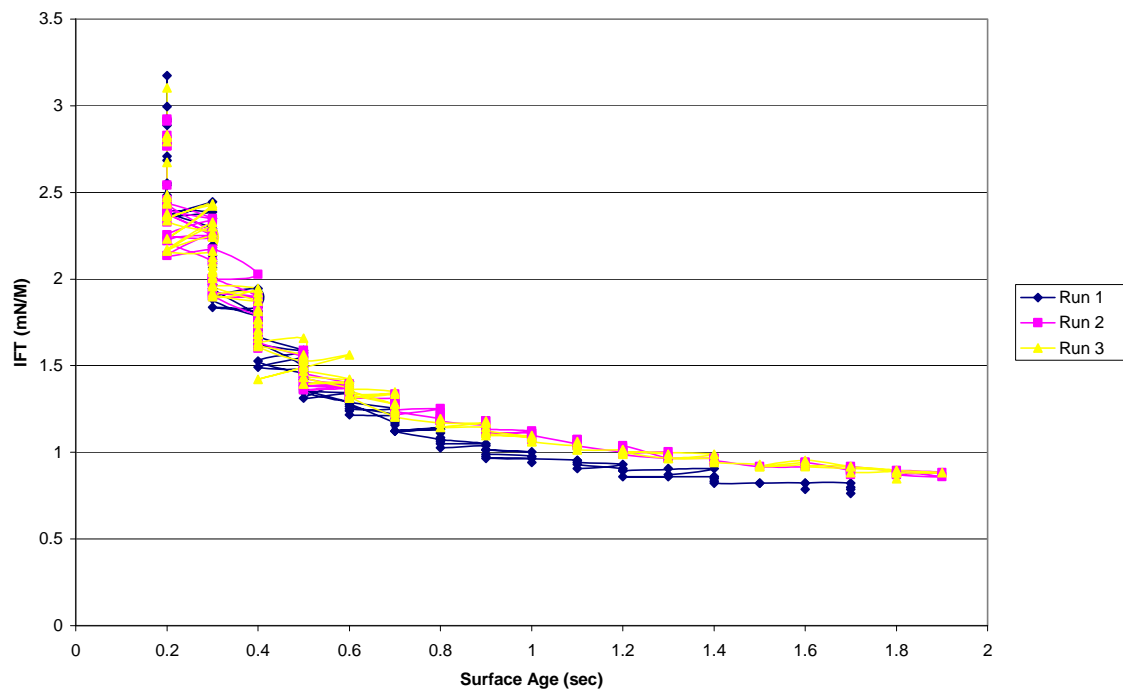
IFT Ascending Drop, Tetradecane vs. 500ppm Triton X165



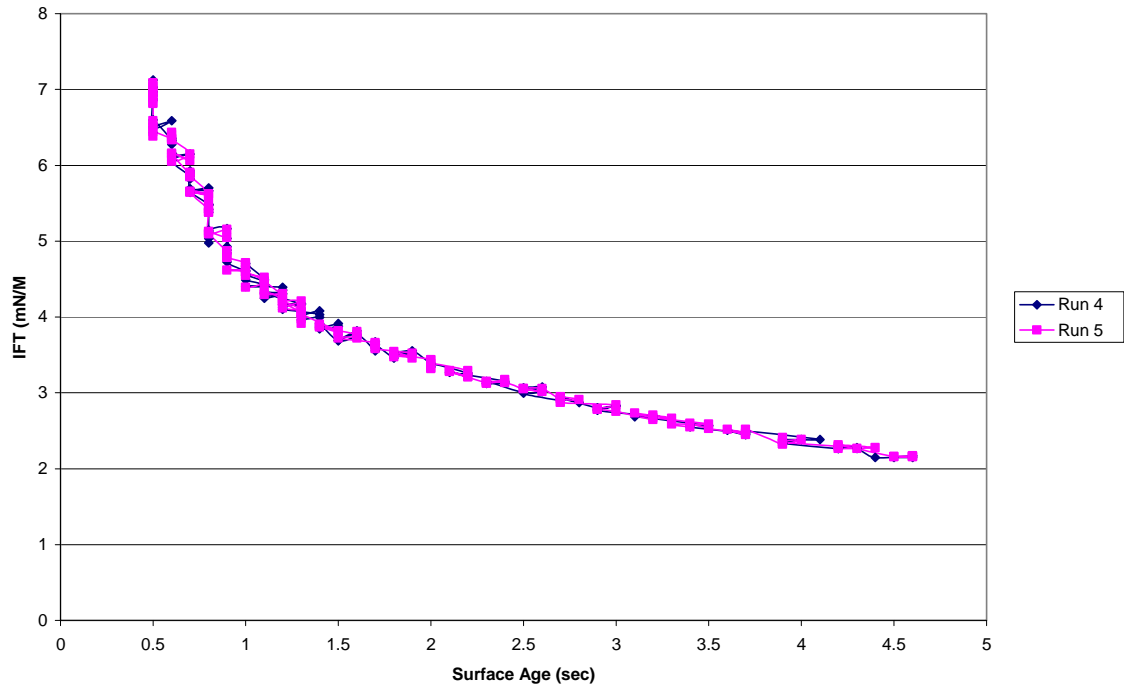
IFT Ascending Drop, Tetradecane vs. 3% Ansul



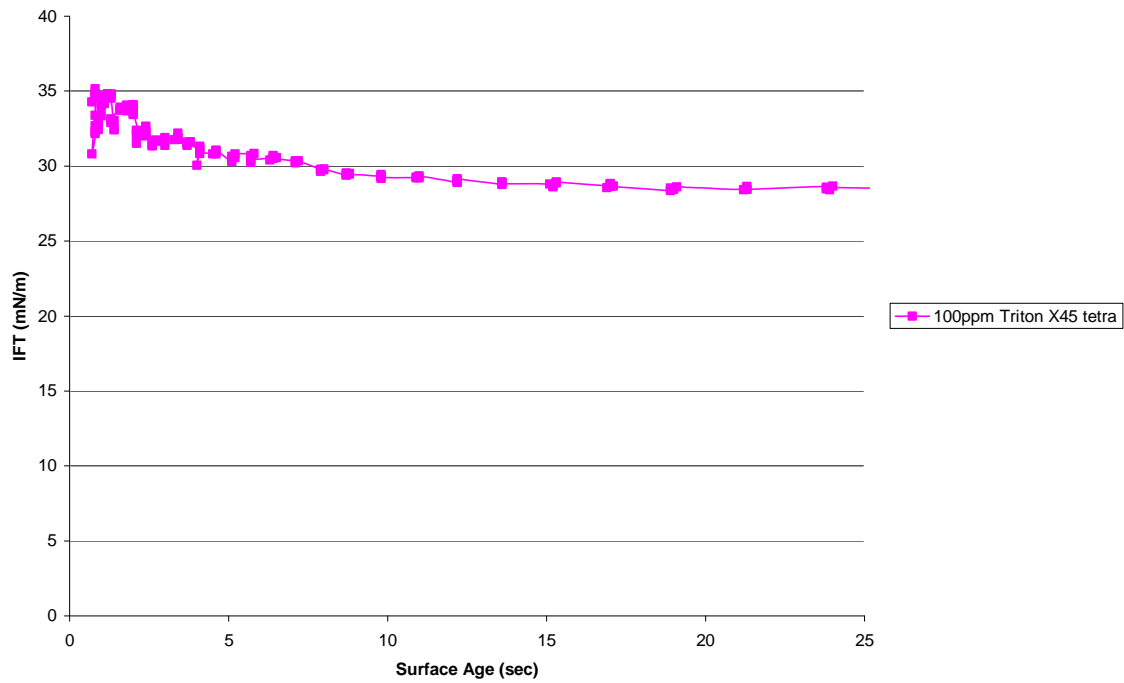
IFT Ascending Drop, Tetradecane vs. 3% National Foam



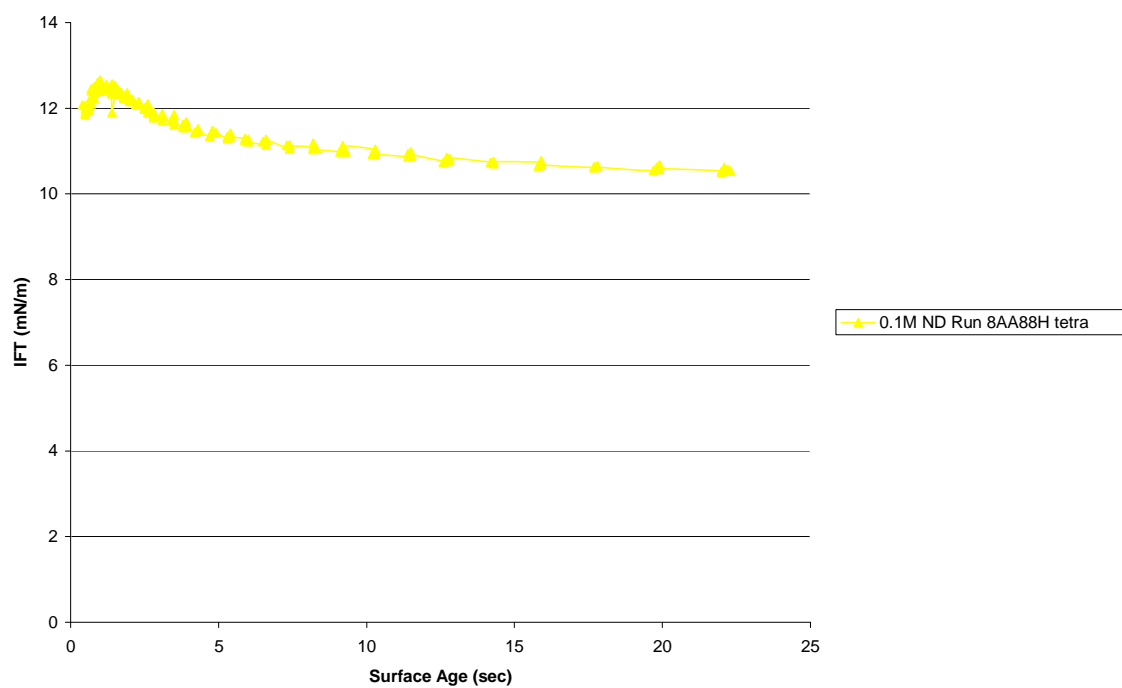
IFT Ascending Drop, Tetradecane vs. 3M



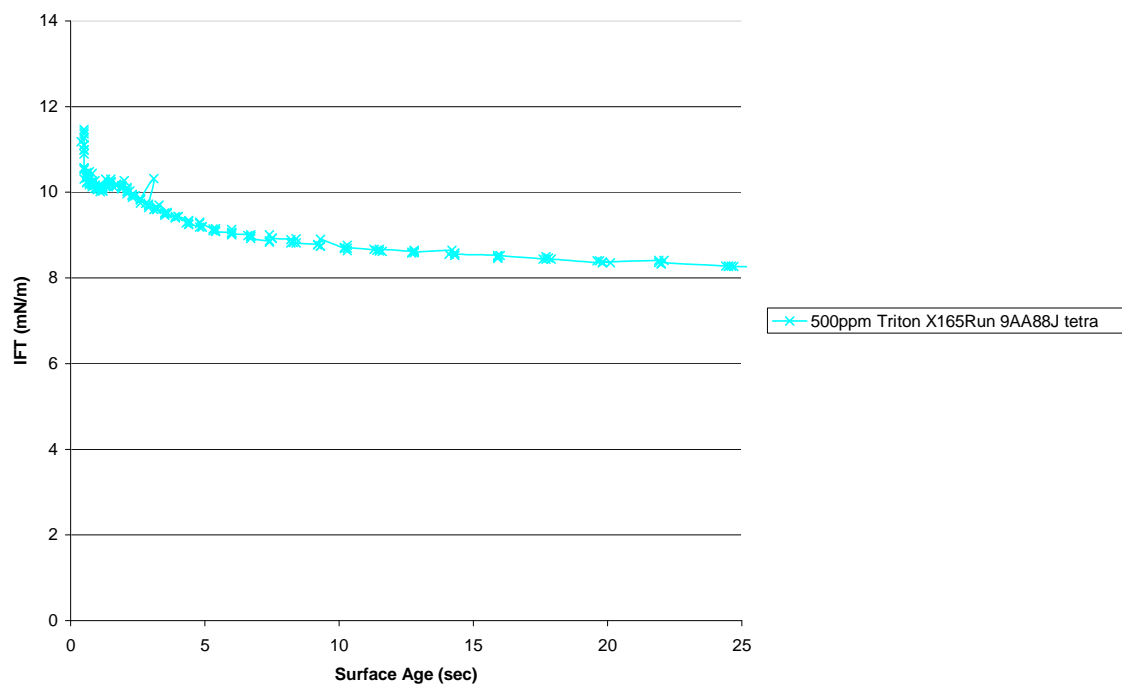
Tetradecane IFT Falling Drop



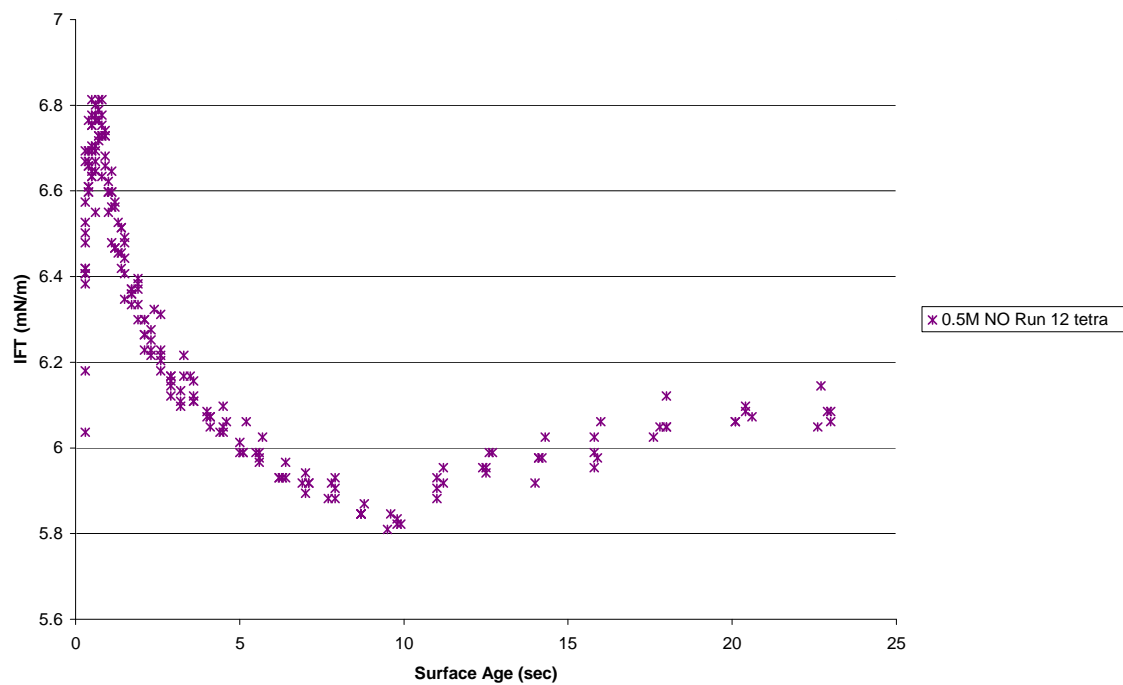
Tetradecane IFT Falling Drop



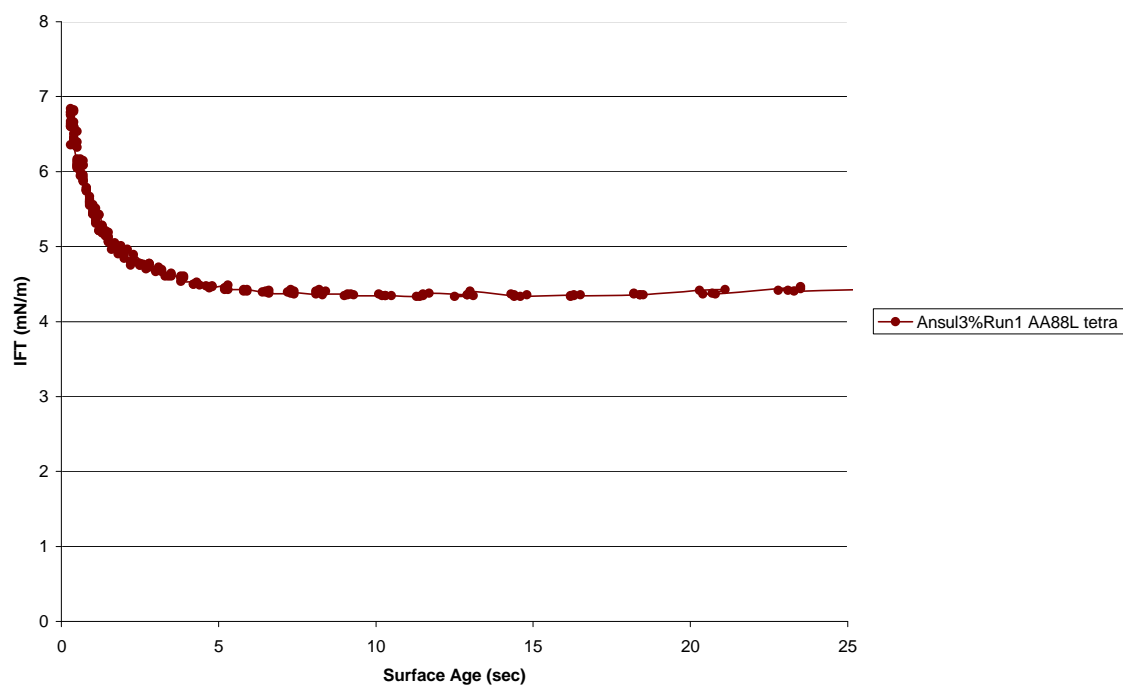
Tetradecane IFT Falling Drop



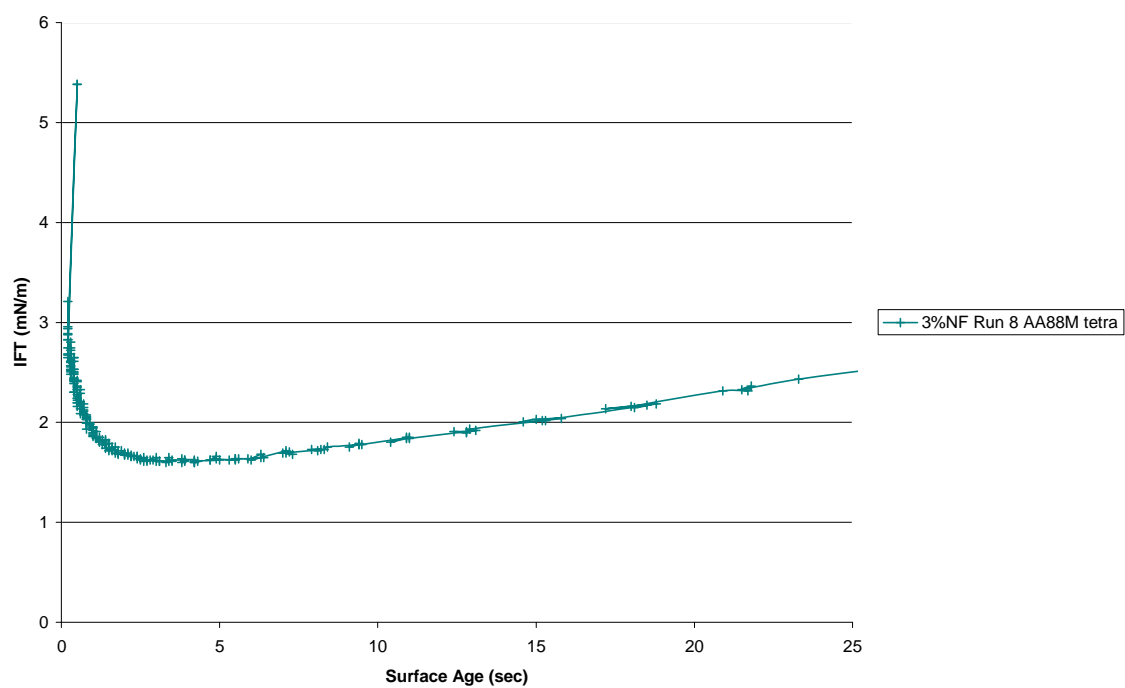
Tetradecane IFT Falling Drop



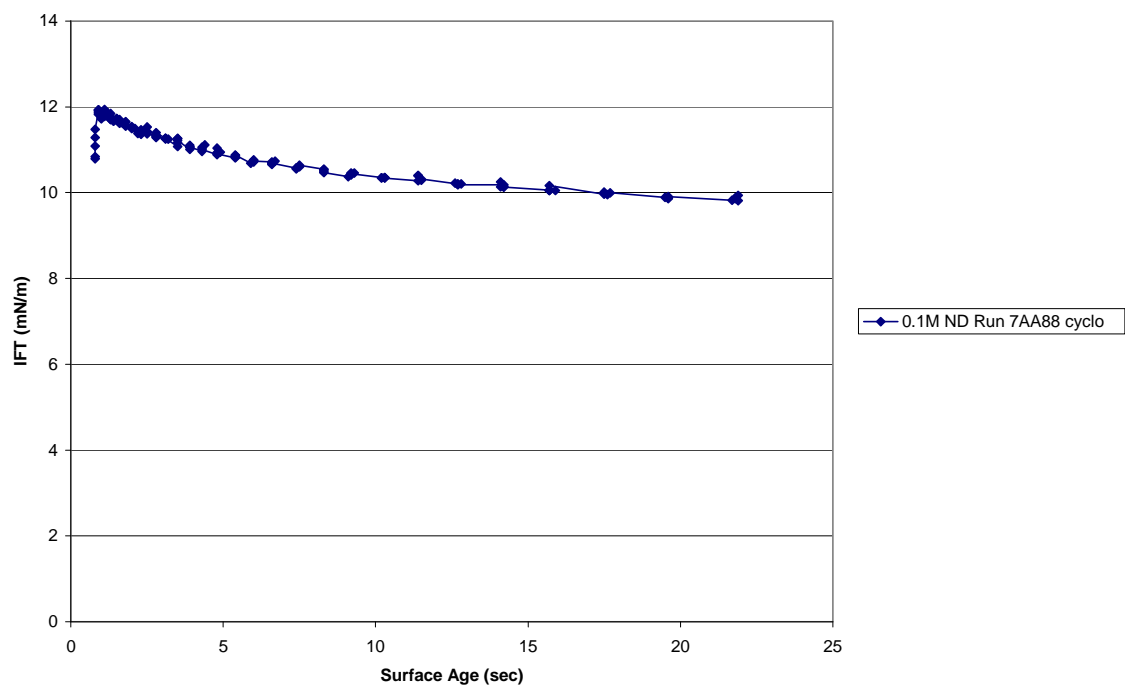
Tetradecane IFT Falling Drop

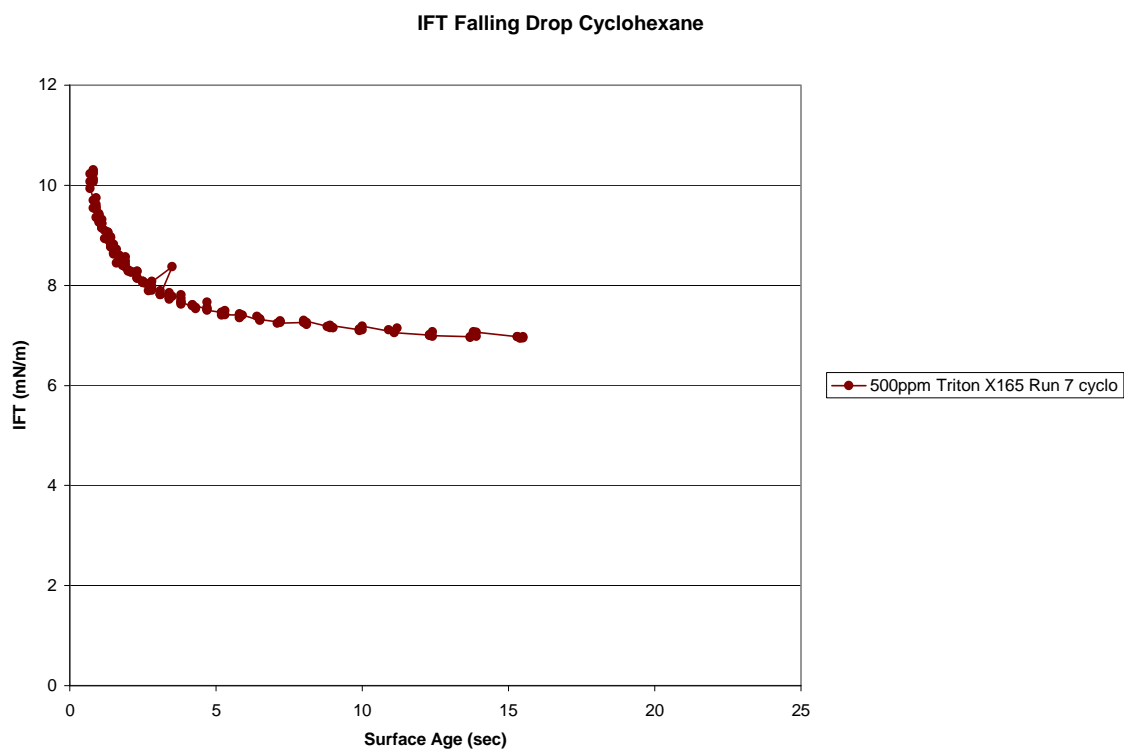
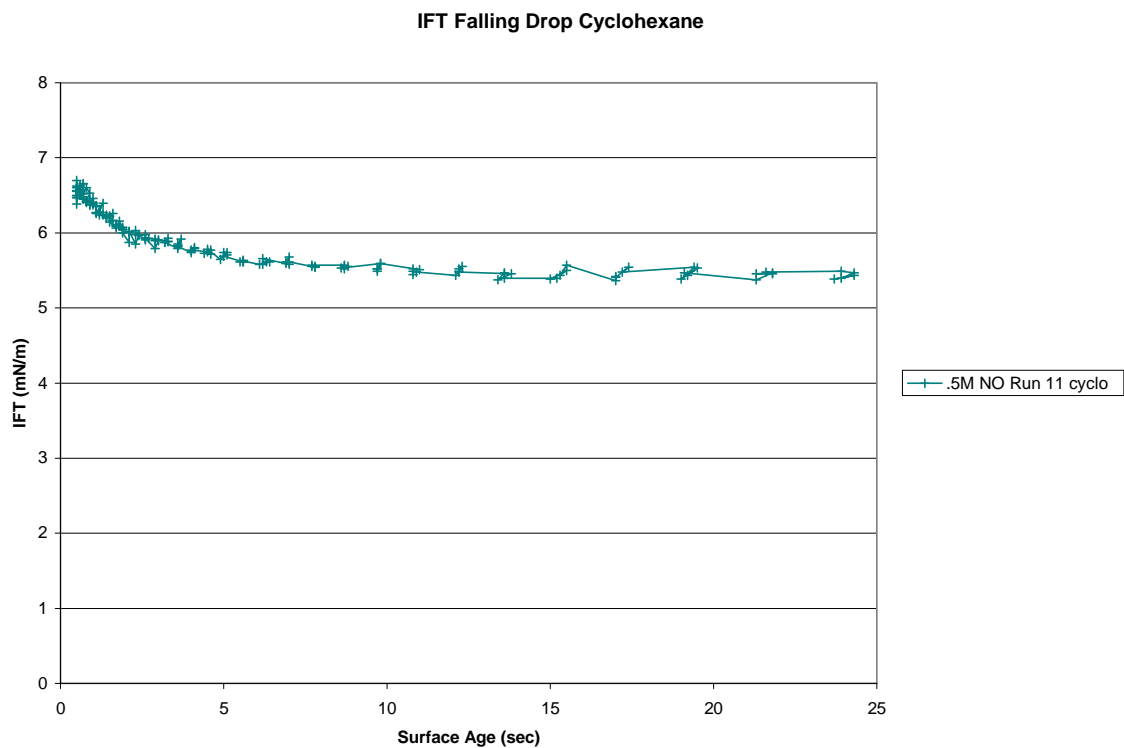


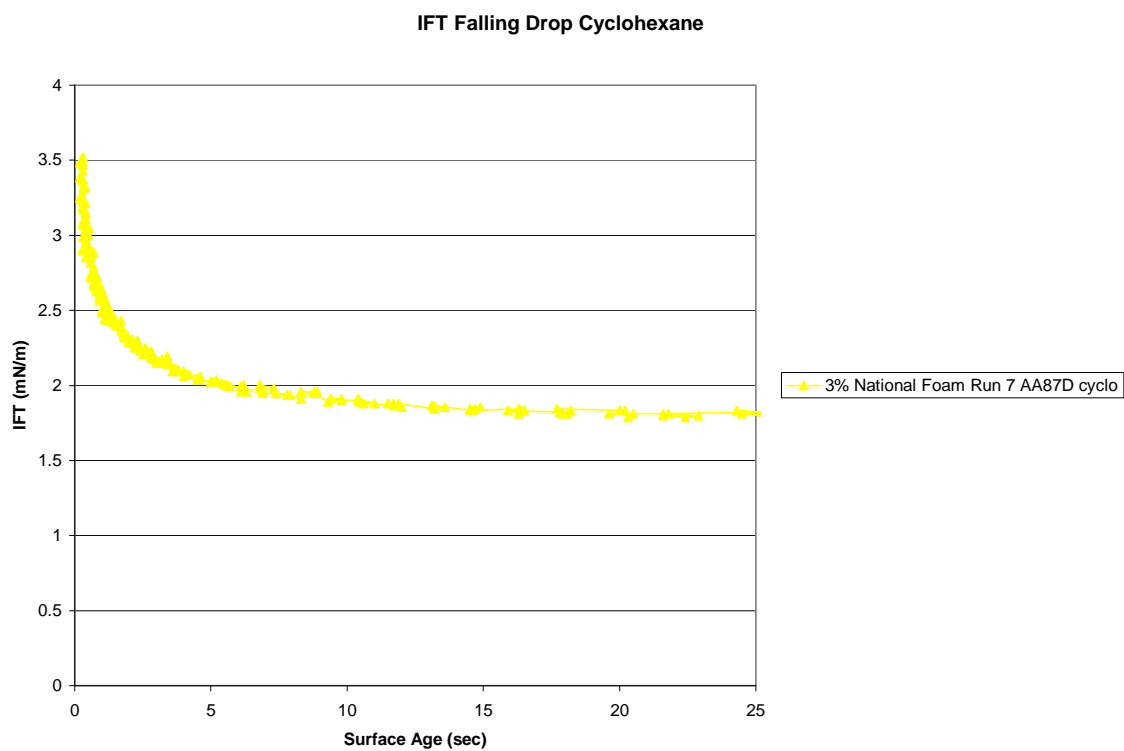
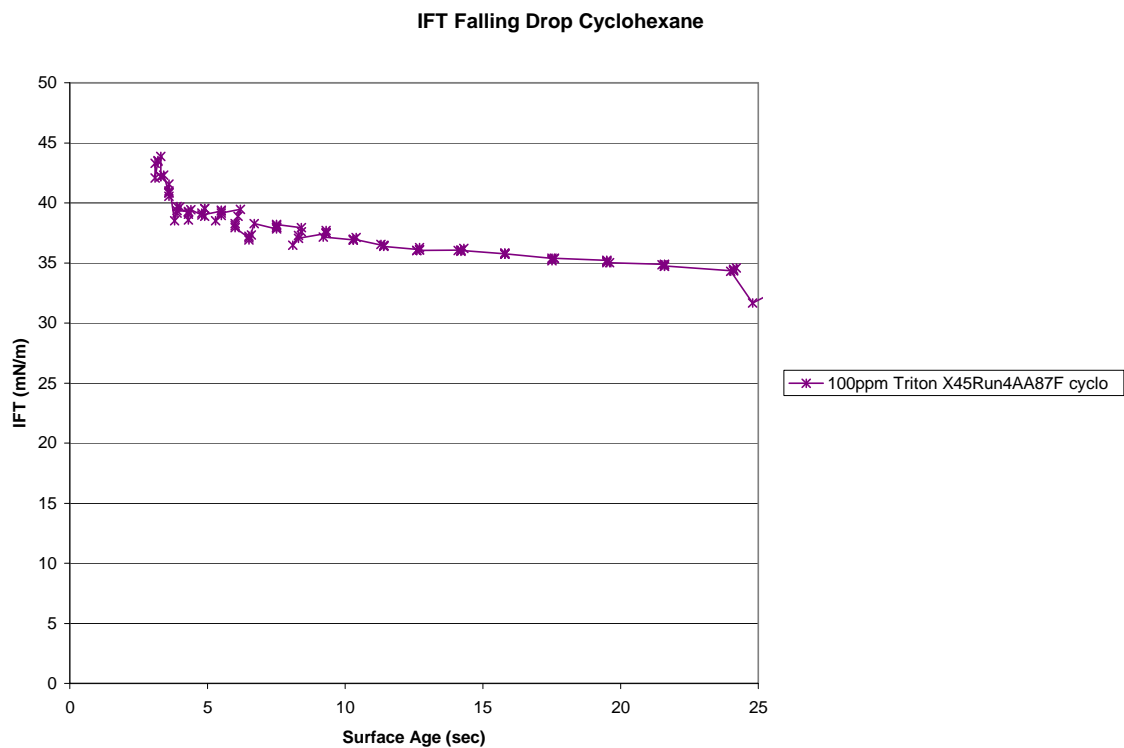
Tetradecane IFT Falling Drop



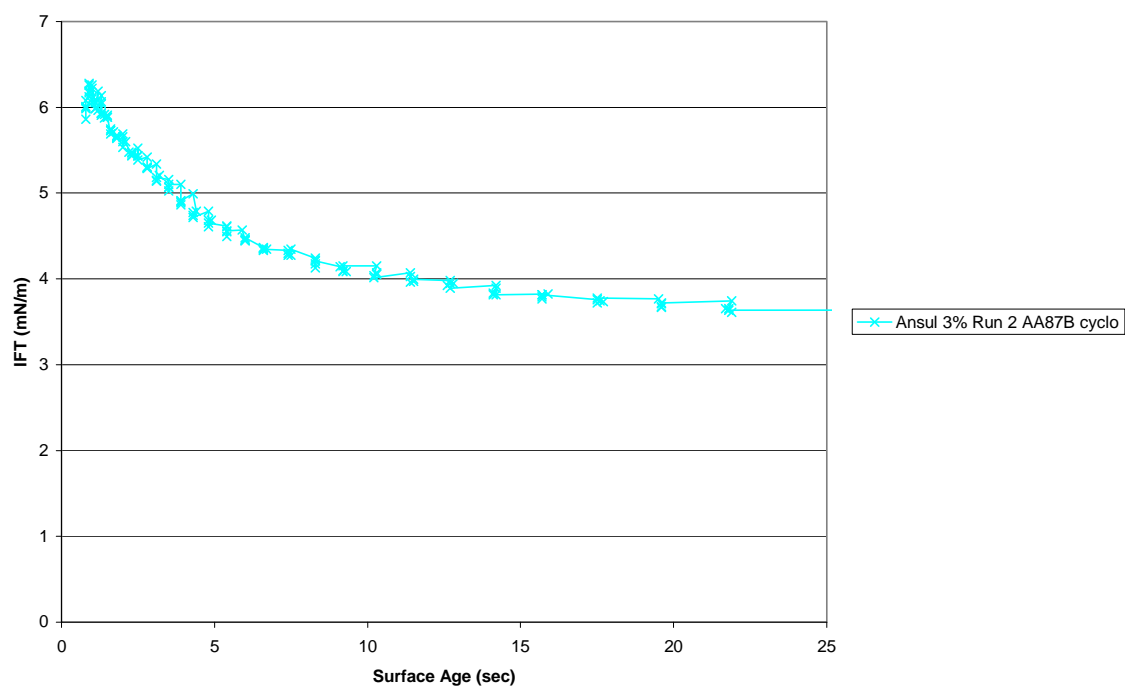
IFT Falling Drop Cyclohexane



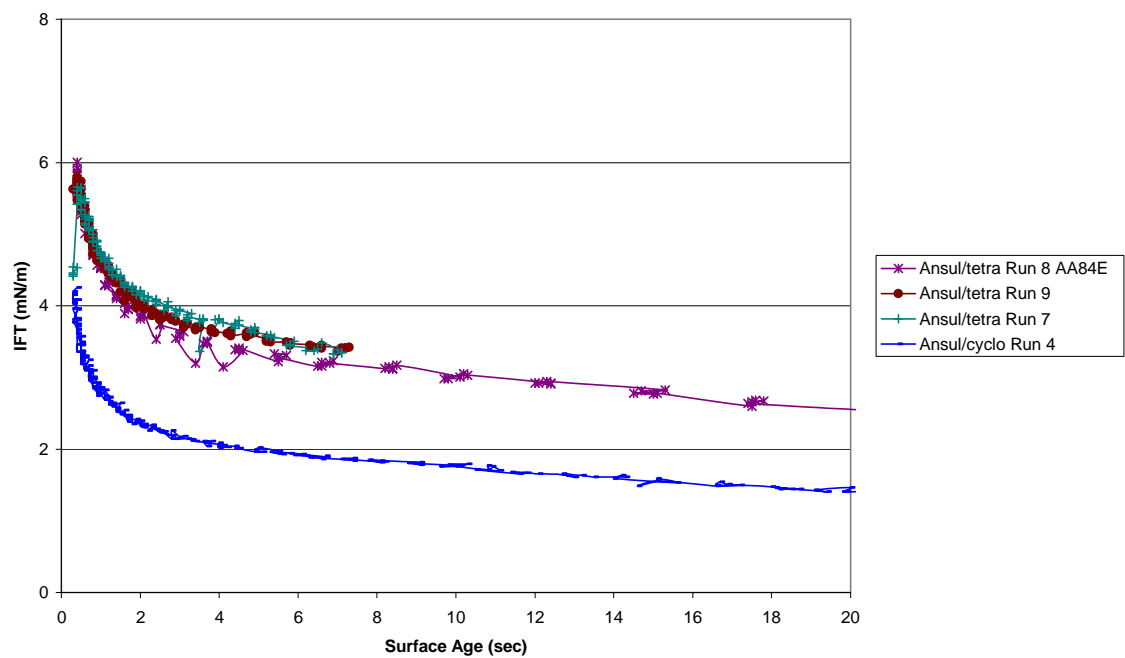




IFT Falling Drop Cyclohexane



IFT Ascending drop, Comparison between Cyclohexane and tetradecane as Dispensing Liquid



IFT Ascending drop, Comparison between Cyclohexane and tetradecane as Dispensing Liquid

